Advances in Polymer Chemistry

Edited by V. V. KORSHAK

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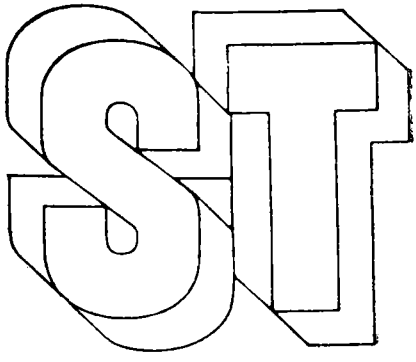

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Mem. USSR Acad. Sci.

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Прогресс полимерной химии в СССР
Под редакцией В.В. Коршака

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Preface

Polymer chemistry belongs to the group of sciences that are developing rapidly in the Soviet Union. Therefore, in an attempt to give a brief overview of the current state and fundamental directions in the development of the field of polymer chemistry in the USSR, one immediately sees the limited means available to us, the help of which is necessary to grasp the enormous volume of knowledge which is characteristic for the given field. This demands that we limit ourselves, at the very least, to individual examples and illustrations of only the most important aspects of Soviet polymer science.

Polymer science in the USSR includes a number of developed directions, both in the area of polymer synthesis, as well as in the area of their chemical and physical modifications. It is particularly important to note that along with the rapid development of chemical directions, great progress is being made in this country in the area of physical chemistry and chemistry of polymers. This provides the opportunity for the successful development of modern processes of conversion and use of polymers, as well as for the manufacture of various items from them.

Among the theoretical issues of polymer chemistry, of essential significance is the problem of the chemical heterogeneity of polymers arising as a result of the presence of anomalous units in macromolecules. Anomalous units and, consequently, chemical heterogeneity of polymers arise primarily as a result of reactions of synthesis and modification of polymers, and they lead to a change in the complex of properties of high-molecular compounds.

Great development in the work of Soviet scientists has been accomplished in the research in the area of reactions of polycondensation. Such research led to the clarification of the mechanism of such processes and the creation of a series of new methods of polymer synthesis with the use of highly efficient catalysts.

Polycondensation reactions were used widely as a method for synthesizing a great number of new polymers. Among the polymers synthesized by us, "carbin" is particularly interesting. "Carbin" is the third, earlier unknown form of elementary carbon, which, as opposed to diamonds and graphite, has linear macromolecules and therefore differs fundamentally in its properties.

Fundamental research has been conducted during the synthesis and study of polymers with specific properties, including thermally

stable organoelement, conducting, and semiconductor polymers, as well as others. As a result of these investigations, various polymers with a wide spectrum of properties were obtained and found to have various practical applications.

No less interesting were the investigations into the stabilization of polymers, which allowed us to slow down the ageing and extend the service life of polymers.

It is worth noting the great volume of work done in the area of obtaining polymers via the polymerization of heterocycles and the polycyclotrimerization of monomers with triple bonds. Research in these areas allowed obtaining a number of new polymer structures and the mechanism of these reactions was studied. As a result, new activators of polymerizational processes were found, which enabled us to obtain more thermostable and stable polymers containing nitrogen in various combinations.

Soviet scientists devoted a great deal of attention to the processes of interaction between polymers and various mineral and organic fillers which occur intensively, for example, during the processes of friction. On the basis of these works, the concept of tribochemistry as a new branch of polymer science was formulated.

The research in the area of organoelement polymers was also greatly developed, and represents the leading direction of the future development of polymer synthesis. At the present time, there are already more than 40 elements used in synthesis research, and this list is continually growing.

In this monograph, some of the directions mentioned in this preface are discussed, and we hope that this will help the reader gain an understanding of the successes and tendencies in the development of Soviet polymer science.

Professor V.V. Korshak,
Member of the USSR Academy
of Sciences

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1 The Development of Polymers in the Soviet Union

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1. INTRODUCTION

One of the branches of chemistry that is making extremely rapid progress is the chemistry of polymers, since the advancement of the most important industries is dependent on the manufacture of high molecular weight compounds such as plastics, synthetic rubbers, fibres, and film formers. New high-strength heat- and fire-resistant materials and also many cheap and high-quality materials for making domestic appliances can be obtained from synthetic polymers.

A significant contribution to the creation of the science on polymers was made by Russian chemists. The chemistry of high molecular weight compounds in the USSR developed through the investigations of well-known scientists such as A. M. Butlerov, V.V. Markovnikov, S.V. Lebedev, A.E. Favorsky, V.N. Ipat'ev, P.P. Shorygin, N.D. Zelinsky, and G.S. Petrov. However, there had been not a single scientific establishment in Russia founded specially to investigate high molecular weight compounds; neither a single monograph nor a manual on this issue had ever been published.

Research establishments came into existence in the Soviet times. They participated in creating and putting to production synthetic rubber, plastics, artificial and synthetic fibres, varnishes, and dyes. The Laboratory of High Molecular Weight Compounds was set up in 1934 under the auspices of the Academy of Sciences and in 1935 it became an integral part of the Institute of Organic Chemistry of the USSR Academy of Sciences, in which basic research was carried out on the synthesis of monomers and polymers, including organoelement ones. Great attention was given to the study of new types of synthetic rubbers and to expanding the variety of available monomers. Research into polycondensation carried out in the 1940-1950s laid down theoretical fundamentals of this process.

The Laboratory of Chemical Physics began functioning independently in 1935. It was transformed into the Institute of Chemical Physics, became a research centre in the creation of chain reaction theory the theoretical fundamentals of radical polymerization. Studies were carried out on the polymerization of various monomers including cyclic and carbonyl-containing compounds, and the problems of destruction and stabilization of polymers were developed.

Over the period of 1925 - 1935 the basic conceptions were formed on a macromolecule, polymerization and polycondensation, polymerhomology and polymeranalogy, molecular weight, the degree of polymerization, and the like. As a result, the objects of research of the chemistry of high molecular weight compounds were found to differ from those of classical organic and colloid chemistry; this gives now every reason to refer to the former as the science on polymers.

The science on polymers in the USSR was making progress in various aspects: alongside the preparation and investigation of polymers, the mechanisms of synthesis and transformation of high molecular weight compounds was studied. An insight into the essence of the processes under investigation so as to master and control them is a typical feature of research work in the Soviet Union. This was the main cause for the advancement in the chemistry of polymers.

The investigations carried out by scientists using chemical, physical and physicochemical methods have revealed typical features of the structure and properties of polymers. Their cognition is of great practical importance.

The first outstanding achievement in this field had been the synthesis of butadiene-base rubber carried out on an industrial scale using the S.V. Lebedev method in the early 1930s. Later on the Soviet Union started the world's first industrial production of *cis*-polyisoprene rubber, a synthetic analogue of natural rubber.

The Soviet chemistry of high molecular weight compounds has successfully solved the fundamental problems of free-radical polymerization of unsaturated compounds, thus making it possible to establish the principles of controlling the polymerization processes and the means for synthesizing various new polymers. N.N. Semenov, S.S. Medvedev, B.A. Dolgoplosk, S.N. Ushakov, and other researchers took an active part in the solution to these problems.

A great contribution to the emergence and development of the chemistry of polymers containing inorganic molecular chains has been made by K.A. Andrianov whose research work helped starting the manufacture of organosilicon polymers in the 1940s.

The Institute of High Molecular Weight Compounds of the USSR Academy of Sciences was founded in Leningrad in 1948. Here extensive research was carried out on the synthesis of new types of rubbers, with a view to creating and putting to production high-quality synthetic stereoregular rubbers; the theory on stereospecific polymerization was developed, new catalysts and polymerization initiators were developed, and the kinetics and the mechanism of macromolecule formation were studied. The synthesis of cyclochain polymers and physiologically active polymers deserves special attention.

The Institute of Petrochemical Synthesis of the USSR Academy of Sciences was founded in 1948 where theory of ionic and stereospo-

clic polymerization was developed, and research was made to expand a variety of monomers by directly using petrochemical raw materials in their manufacture, and also to obtain new organosilicon monomers and polymers based on these monomers.

In 1954 the N.D. Zelinsky Institute of Organic Chemistry of the USSR Academy of Sciences branched off into an Institute of Organoelement Compounds of the USSR Academy of Sciences in which research was continued to synthesize organoelement monomers and polymers based on these monomers.

The Soviet scientists V.V. Korshak, S.R. Rafikov, L.B. Sokolov, and G.S. Kolesnikov carried out research into polycondensation; the research revealed wide prospects of this method of synthesis of high molecular weight compounds, its regularities, and various synthetic possibilities.

Great progress has been made by Soviet scientists in the investigation of the polymer structure as related to its properties. A major contribution to the solution of this problem was made by V.A. Kargin's works which made it possible to tackle the problems of modification of polymer properties and new methods of processing polymers into articles.

The work on the chemistry of high molecular weight compounds was carried out in two trends; the latter related, firstly, to the preparation of polymers from low molecular weight compounds by polymerization or polycondensation and, secondly, to the modification of the polymers thus prepared by substitution, cross-linking or exchange reactions.

2. POLYMERIZATION

The ability of molecules of unsaturated compounds to enter into polymerization reactions was discovered by A.M. Butlerov in 1875. In 1900 I.L. Kondakov, Butlerov's pupil, was the first to obtain synthetic rubber by polymerization of dimethylbutadiene. The works of A.E. Favorsky, Butlerov's another pupil, played a big role in the polymerization of unsaturated hydrocarbons.

From the works devoted to the study of the mechanism of polymerization, special emphasis should be placed on N.N. Semenov's works on the theory of chain reactions. His monograph "Chain Reactions" (1934) won the D.I. Mendeleev prize in 1936 [1].

The theory of chain reactions permitted elucidation of the mechanism of reactions of polymerization and depolymerization, cross-linking of polymers, photolysis, polymer destruction induced by high-energy radiation and mechanical loads, and polymer ageing.

N.N. Semenov's further works on the theory of chain reactions (see, for example, Ref. [2]) was highly acclaimed, and he was awarded the State prize in 1941, and the Nobel prize in 1956.

2.1. Radical Polymerization

In the mid 1930s, S.S. Medvedev began systematic studies of the chain mechanism of radical polymerization reactions. He established the radical nature of many polymerization processes, formulated the concept of initiation of polymerization as the emergence of chains owing to the decomposition of peroxide compounds to form free radicals. He gave the first quantitative kinetic formulation for chain-transfer reactions, which determined their importance for controlling the molecular weight of polymers, and he made a substantial contribution to elucidation of the mechanism of radical polymerization when deep conversions, copolymerization, and emulsion polymerization occur.

While investigating the kinetics of polymerization of chloroprene in the presence of peroxides, S.S. Medvedev showed that free radicals are intermediates in the polymerization process which actively participate in the development of chain transformations [3]. He developed a quantitative approach for determining free radicals and the mechanism for the formation of branched polymers. He was awarded the State prize for his research work in 1946.

To find a solution to the major problem on the nature of growth of the polymer chain in the course of radical polymerization, a big role was played by the works of S.V. Lebedev [4] who investigated rubber synthesis reactions. In the 1950s, the problem on the addition of a monomer to the growing chain was dealt with in the works of B.A. Dolgoplosk, A.A. Korotkov, and their co-workers [5].

The development of research into radical polymerization showed that polymer chain growth is complicated by different side reactions. S.S. Medvedev found that as polymerization of styrene occurs in aromatic hydrocarbons, the growing free radical may interact with a solvent. This leads to a change in the direction of the process and to chain termination by a solvent or an impurity [6].

Kh.S. Bagdasar'yan's pioneer research into photopolymerization contributed to establishing the basic regularities of this process and proved to be a major stage in the development of polymerization theory [7].

The effect of steric hindrances caused by the substituents at the double bond of ethylene hydrocarbons on the polymerization process is revealed in the works of V.V. Korshak [8]. The substituents in the ring were found to have an effect on the polymerization process, which is much less than that of the substituents at the double bond of ethylene hydrocarbons, this effect being dependent on the type of polymerization. For example, this effect is stronger in radical polymerization than in ionic polymerization.

In the 1950s, the chemists' attention was drawn to emulsion polymerization [9]. The works of S.S. Medvedev, B.A. Dolgoplosk,

A.N. Pravednikov, and B.A. Dogadkin played a considerable role in establishing the common tendencies of polymerization in emulsion systems.

In the 1960s, the research carried out by V.A. Kargin and V.A. Kabanov [10] laid the basis for a new trend in the chemistry of polymerization processes. This trend resided in preliminary chemical activation of monomers by binding them into complexes and subsequent polymerization of the latter. Polymers of the previously unknown polymer classes (such as polynitriles, polypyridine, and polyquinoline) had been synthesized in this manner.

The quantitative investigation of the influence of complexing agents on individual elementary acts of radical polymerization and copolymerization carried out by V.A. Kabanov and V.P. Zubov permitted developing the mechanism of complex-radical polymerization when the complexing agent acts as a catalyst at individual stages of the complex reaction [11]. The investigation of radical polymerization of ionogenic monomers showed that this polymerization is analogous to ionic and coordination-ionic polymerization processes. This allows controlling efficiently the synthesis of polyelectrolytes [10]. The previously unknown reactions, more particularly the Zwitter-ionic polymerization of vinylpyridine salts, were carried out and studied.

The successful development of experimental research into the influence of complex formation on chain growth in homo- and copolymerization led to revealing continuous homogeneous radical polymerization of some vinyl monomers in liquid media [11].

The investigation of rapid low-temperature polymerization of solid monomers during glass-crystal phase transformations was essential in the creation of current concepts on the kinetics and topochemistry of solid-phase polymerization [12].

In the 1970s, V.I. Gol'dansky investigated the polymerization processes that occur during devitrification of glassy monomer solutions radiolized at —196 °C [13]. It was shown that conditions for effective growth of macromolecules can be maintained at almost suppressed recombination termination of macromolecules.

Investigations of the mechanism of chain polymerization at superlow temperatures carried out by A.D. Abkin and V.I. Gol'dansky are of great interest [14, 15]. The study of radiation polymerization of tetrafluoroethylene, acrolein, formaldehyde, and other monomers at a temperature from —130 to —270 K has led to the discovery of the phenomenon of a low-temperature limit in the rate of chemical reactions.

Important results were obtained in the 1970s when studying the ways of using polyfunctional initiators and low-efficient inhibitors when radical polymerization occurs [16, 17]. It was shown that polymers containing terminal functional groups and peroxide groups in

the side chains can be obtained using polyfunctional initiators. These polymers are promising in practical terms. The theoretical analysis of polymerization induced by polyfunctional initiators has led to the methods of synthesizing high molecular weight compounds having the desired characteristics and properties [18].

The study of the polymerization of polyhalosubstituted unsaturated monomers carried out by A.P. Suprun and his co-workers appears to be one of the interesting trends in radical polymerization [19 - 21]. The use of high pressure enabled the authors, while varying the ratio of reaction rates of chain growth, chain terminations, and radical isomerization, to control the kinetics of the process and to obtain polymers of the desired structure.

In the 1970s, research into radical polymerization in liquid-crystalline media was undertaken. Yu.B. Amerik, B.A. Krentsel, N.A. Plate, V.P. Shibaev, and their co-workers established that the occurrence of the reaction in an anisotropic system not only affects the kinetics of the process, but also permits controlling the spatial microstructure of the polymers obtained [22, 23].

2.2. Ionic Polymerization

In the investigation of ionic polymerization of unsaturated compounds, S.S. Medvedev *et al.* established in the 1940s that the intermediate product was a carbonium ion [24]. The carbonium ion is always within the field of its counterion in low-polar solvents to form an ion pair. S.S. Medvedev was the first to show the possibility of performing anionic polymerization and preparing "living" polymers.

In the investigation of relative activity of catalysts in cationic polymerization, S.V. Lebedev and then S.S. Nametkin and other researchers found that the rate and the degree of polymerization were dependent on the state of a sulphuric acid catalyst [25, 26]. While studying the polymerization of olefins in the presence of boron fluoride and its compounds, A.V. Topchiev and his co-workers managed to work out a specific technique for affecting the catalyst activity and thus synthesizing oligomers and polymers of the desired molecular weight [27].

The first works on anionic polymerization in the USSR were done by S.V. Lebedev when he investigated the process for producing synthetic rubber in the presence of metallic sodium as a catalyst [28]. Working in the same trend, S.S. Medvedev studied the kinetics of anionic polymerization. Researchers at the Institute of High Molecular Weight Compounds took part in working out this polymerization [29 - 30]. The attention was mainly directed to the problem of polymerization initiation with organic derivatives of alkali metals. S.S. Medvedev, A.A. Korotkov, *et al.* hold that the nature

of an alkali metal in metal alkalide and the reaction medium exert a certain influence on the kinetics of polymerization, the composition, and the structure of the resulting polymer.

After Ziegler and Natta discovered complex catalysts, a number of new chain stereospecific polymerization processes were discovered. A great contribution to investigating these processes was made by S.S. Medvedev, B.A. Dolgoplosk, A.A. Korotkov, G.A. Razuvaev, and A.V. Topchiev. The important investigations of experimental and theoretical nature carried out by these scientists enabled them to establish that the high activity and stereospecificity of these catalysts are caused by alkylation, ionization of the transition metal, and coordination of olefin on the latter. In addition, the nature of the active centre, namely the transition metal ion and its ligand environment, in complex catalysts determines the rate of elementary acts and the microstructure of the resulting macromolecule.

In A.V. Topchiev's view, Ziegler catalyst polymerization involved alkylation of titanium tetrachloride with organoaluminium compounds to form catalytically active organic titanium derivatives [31]. To elucidate the role of titanium compounds in complex catalysts in the polymerization of propylene, G.A. Razuvaev replaced titanium halides by other titanium compounds [32]. The reducing capacity of organoaluminium compounds with respect to titanium tetrachloride was also studied by A.A. Korotkov and B.A. Dolgoplosk [33].

As a result of the theoretical research into stereospecific polymerization, A.V. Topchiev and his co-workers at the Institute of Petrochemical Synthesis obtained stereoregular polyisobutylene and sulphochlorinated polypropylene [34], and the research team headed by V.A. Kargin synthesized stereoregular polystyrene and polymethylmethacrylate [35].

In the 1970s, B.A. Dolgoplosk managed to establish that organometallic compounds of transition metals with a π-allyl bond and a σ-carbon-metal bond appear to be active centres in the stereospecific polymerization of dienes [36 - 38]. In the investigation of catalysis for polymerization processes carried out by individual organometallic compounds, B.A. Dolgoplosk and his co-workers determined the nature of the active centres that are responsible for stereoregulation. It was found that all the possible microstructures having high selective activity may be realized on the same metal depending on the nature of ligands that surround it. The mechanism of stereoregulation in coordination polymerization and the regularities of stereospecific copolymerization induced by coordination systems were found. This allowed assessing the relative reactivity and mutual influence of monomers on the chain microstructure. Lanthanide-base catalysts were used to advantage for the preparation of *cis*-polymers and copolymers of dienes.

Using organochromium compounds as an example, as the polymerization process proceeds due to chemical bondage of these compounds with the surface of aluminosilicate or silica gel, the mechanism of the formation of *trans*-polymers and copolymers of dienes was investigated. Organometallic catalysis on the surface also opens new prospects for the polymerization of olefins.

According to the investigations carried out by B.A. Dolgoplosk *et al.*, reactions of cycloolefin opening and olefin metathesis represent a chain process. It involves new types of active centres, i.e. carbenes-transition metal complexes [39, 40].

In the 1970s, proceeding from the above-stated conceptions on the structure of active centres, S.R. Rafikov showed the effect of the transition metal and its ligand environment on the polydiene microstructure and the rate of ionic-coordination polymerization of α-olefins and dienes [41, 42]. For example, as electronegativity of the ligand at the titanium atom increases, the number of 1,4-*cis* units in the polydienes decreases. Unlike titanium catalysts, when the polymerization of dienes occurs in the presence of the lanthanum subgroup compounds, the nature of the cation and its ligand environment practically exert no influence on the polydiene microstructure which contains predominantly 1,4-*cis* units.

2.3. Ionic Polymerization of Heterocycles

Great progress has been made by Soviet scientists in the investigation of the processes of ionic polymerization of heterocyclic monomers, and the research was aimed at accumulation of factual material and its theoretical generalization.

From the 1960s, V.V. Korshak and T.M. Frunze carried out extensive research into activated anionic polymerization of lactams. It is very important as the method for the chemical formation of polyamides by the monomer-article scheme without the polymer-processing stage [43, 44]. The use of various activators makes it possible to control the polymer chain growth, and to exert the influence on the molecular structure and properties of the polyamides obtained.

In recent years T.M. Frunze and his co-workers have investigated the kinetic regularities of synthesis of polycaproamides using a method of activated anionic polymerization of ε-caprolactam when polymerization and crystallization of the resulting polymer were carried out simultaneously [45]. The process of polymerization of ε-caprolactam was found to be of autocatalytic nature and the cause of this phenomenon was established to be solvation of the active centres by the resulting polymer chain.

The significant results were obtained by N.S. Enikolopov when he studied in detail the process for synthesizing polyformaldehyde and

copolymers of formaldehyde from oxygen-containing monomers [46]. The investigations of the processes of formation and of the properties of heterochain polymers prepared by ionic polymerization of heterocycles by V.A. Ponomarenko revealed that polymer chain units adjacent directly to the active centres exert a great effect on the reaction mechanism [47]. In anionic and coordination-anionic processes they form an asymmetric coordination sphere around the counterion or metal. This sphere resembles the right and left spirals of polypeptides and determines the stereospecificity of the process. The developed concepts on the structure of these active centres allow elucidating in a new manner the regularities of anionic and coordination-anionic polymerization of not only oxyranes, but also sulphur- and nitrogen-containing heterocycles.

S.G. Entelis' works were devoted to the investigation of the ionic polymerization of oxygen-containing heterocycles. They laid the basis for creating scientifically substantiated approaches to the controlled synthesis of polymer binders having a complex of the predetermined physicochemical properties [48]. These works dealt with the process of solvation of the active centres in these and other systems by the chain fragments.

Systematic investigations of the polymerization of cyclic organosilicon compounds were carried out by K.A. Andrianov, more particularly he has developed methods for synthesizing polyfunctional initiators which were used to obtain high polymers of star-like structure [49].

The concepts on the mechanism of anionic polymerization of organosiloxane cycles, as put forward by K.A. Andrianov, are based on the hypothesis of complex formation between organocyclosiloxanes and nucleophilic reactants. As a result of the investigation of the effect of the concentration of initiators and the duration of polymerization of cyclosiloxanes on polymer polydispersity, conditions were found for synthesizing polyorganosiloxanes having a polydispersity coefficient close to unity [50].

In the last decade N.S. Enikolopov and his co-workers have obtained fundamental results when they investigated the processes for formation and transformations of polymers under extremal conditions of stress-induced plastic flow [51]. Under these conditions, the polymerization of solid-state monomers proceeds abnormally rapidly and virtually without activation energy. More particularly, the rate constants of polymer chain growth is 8 to 10 orders of magnitude higher than analogous ones when liquid-phase reactions are carried out under the same pressures.

N.S. Enikolopov carried out research to improve efficiency of industrial processes for synthesizing the major polymerization polymers and studied the theory of polymerization reactors [52]. One of the variants of this theory was applied to model the processes of

block polymerisation of styrene taking into account the kinetic and structural aspects of this problem, making it possible to increase substantially operation efficiency of industrial units.

2.4. Polycyclotrimerization

In the 1970s, a new method was developed intensively for the preparation of polymers of different structure containing carbo- and heterocycles in the chain, i.e. cyclotrimerization of C—C and C—N multiple bonds [53]. Using monomers with C—N multiple bonds (cyanates, cyanamides, isocyanates, and the like), S.V. Vinogradova, V.A. Pankratov, and their co-workers have studied the basic regularities of the synthesis of polymers [54]. They have found the ways to carry out this reaction with high selectivity and practically with quantitative conversion of the functional groups, thus making it possible to prepare regularly cross-linked polymers with strictly predetermined distances between the cross-linking joints. Thermal and physicomechanical properties of these polymers may be varied within wide ranges by introducing thermally stable aromatic and organoelement radicals of different structure and size as interjoint fragments of the network.

The investigation of the kinetics and thermodynamics of polycyclotrimerization of monomers containing C—N multiple bonds revealed the basic regularities of this process and conditions were found for the reaction to be carried out with high selectivity, thus making it possible to obtain polymers of chemically regular structure [54, 55].

Of great interest is a new process for preparing polymers containing aromatic cycles in the chain by polycyclotrimerization of acetylene compounds in the presence of complex organometallic catalysts. This process was developed by V.A. Sergeev [56, 57]. The Ziegler catalyst-type catalytic system appears to be the most efficient catalyst for the polycyclotrimerization of the monomers mentioned above. The use of this system improves the degree of aromaticity of the polyphenylenes obtained.

The mechanism of this process was studied [58]. The use of a fuel gas (diacetylene) as the polycyclotrimerization starting material, which is a by-product of the synthesis of acetylene from natural gas, opens prospects for synthesizing polyphenylenes on a commercial scale [56].

3. POLYCONDENSATION

Polycondensation as a method for synthesizing high molecular weight compounds was for the first time used in 1833 when Gay-Lussac and Pelouze obtained a polyester from lactic acid [59].

The first study on the kinetics of polycondensation was made in 1881 when N.N. Menshutkin determined the rate of reaction of ethylene glycol with succinic acid [59]. At the beginning of the 20th century, a promising polycondensation process for preparing phenol-formaldehyde polymers was developed on the basis of a "Petrov's contact" catalyst. Those were the first synthetic polymers whose industrial production was started in 1909-1914 [60]. A plant for the manufacture of carbolite (that was the name of a phenolformaldehyde polymer) was commissioned in 1914 in Russia.

Up to the 1940s, experimental research into polycondensation and industrial production of thermosetting polymers (mostly phenol-formaldehyde polymers) were well ahead of theoretical research, thus hindering further advancement of the chemistry of high molecular weight compounds.

Theoretical research into polycondensation was started in the 1940s by the works carried out by V.V. Korshak at the Institute of Organic Chemistry of the USSR Academy of Sciences. He studied polycondensation reactions using the interaction of dicarboxylic acids with diamines and glycols, dichloroethane with aromatic hydrocarbons, dihydrazines with dialdehydes and found the general regularities that determine the molecular weight of the polymer formed and the distribution of macromolecules in molecular weights. It was found that the rule of non-equivalence of the functional groups plays an important role in polycondensation processes. This rule determines the limiting value of the molecular weight of the polycondensation product obtained. V.V. Korshak won the State prize in 1949 for his works on polycondensation processes.

3.1. Equilibrium Polycondensation

The achievements of the last two decades in the chemistry of high molecular weight compounds were attributable in many respects to a new stage in the development of theory and practice of polycondensation processes. During this period a great deal of experimental material on equilibrium (reversible) polycondensation was acquired by Soviet scientists, notably by V.V. Korshak and his school. This material laid the basis for the discovery and formulation of the basic laws of the formation of macromolecules under conditions of equilibrium polycondensation processes [59]. The investigations of equilibrium polycondensation were further developed owing to the synthesis of new thermally stable polyheteroarylenes of cyclochain structure and coordination-type organoelement polymers.

A.N. Pravednikov and his co-workers studied the reaction of anhydrides of tetracarboxylic acids with diamines with a view to synthesizing polyamido acids (prepolymers in the preparation

of polyimides) and the structure of diamine and the nature of solvent were found to have an effect on the equilibrium constant [61]. The investigation of the kinetics and the mechanism of reactions based on the synthesis of aromatic polyimides enabled the authors to establish the interrelationship between the electron affinity of acid anhydrides and their complex-forming and reactivity with respect to aromatic amines [62], the relative role of intramolecular degradation of amido acid linkages when the cyclization of aromatic polyamido acids occurs [63, 64]. The authors studied the mechanism and the kinetics of hydrolysis of amido acid linkages [65] and anhydride groups [66], the influence of the chemical structure of polyamido acids on the kinetics of their cyclization [67].

The works of M.M. Koton, B.A. Zhubanov, S.V. Vinogradova, and their co-workers were devoted to the investigation of the interaction of dianhydrides of tetracarboxylic acids with aromatic diamines and to the synthesis of polyimides [68-74]. As a result, the mechanism of the reaction of preparation of polyimides was established and a new efficient process of their synthesis was developed through single-stage high-temperature polycyclization in solution. The higher molecular weight polyimides are prepared by this method; these polyimides contain practically no non-cyclized unstable amido acid fragments.

S.V. Vinogradova and Ya.S. Vygodsky found an autocatalytic effect of the reaction of formation of polyamido acids. This phenomenon was used as the basis of a catalytic process for preparing polyamido acids and polyimides developed by these authors [73, 74].

3.2. Non-equilibrium Polycondensation

In the 1960s, non-equilibrium polycondensation was intensively studied, in particular the kinetics, the mechanism, and the regularities of the formation of macromolecules of homogeneous and mixed polymers under non-equilibrium conditions. A big contribution to the solution to these problems was made by V.V. Korshak, A.N. Pravednikov, M.M. Koton, S.V. Vinogradova, and L.B. Sokolov who established the basic common tendencies and specific features of non-equilibrium polycondensation processes. As a result of the investigation of the kinetics and the mechanism of acceptor-catalytic polyesterification of dihaloanhydrides of dicarboxylic acids with diols in the presence of tertiary amines, it was possible to reveal the regularities of the reaction and to develop the principles of oriented synthesis of polymers of the predetermined structure and molecular weight [75, 76].

In 1970 conformationally regular polymers of the new type were synthesized by V.V. Korshak, S.V. Vinogradova, and V.A. Vasnev under acceptor-catalytic polycondensation conditions. The

stereotacticity of these polymers is formed in the course of the reaction, and the macromolecules contain regular sequences of certain rotational isomers [76].

Interesting studies into non-equilibrium polycondensation were carried out by L.B. Sokolov and his co-workers who found the specifics of irreversible polycondensation processes, namely the possibility of preparing high molecular weight compounds at a non-equivalent ratio of the starting compounds by gradual addition of one of the monomers into the reaction zone [77, 78]. L.B. Sokolov's works dealt with an original variant of interfacial polycondensation at the liquid-gas interface (gas-phase or gas-liquid polycondensation); he found its regularities and proposed processes for performing interfacial polycondensation on a commercial scale [77]. The investigation of polycondensation in the liquid-liquid systems enabled L.B. Sokolov to substantiate and develop an industrial method, namely emulsion polycondensation [77, 78].

S.I. Kuchanov suggested a general kinetic approach that permits calculating molecular weight distribution of the products of both linear and branched non-equilibrium polycondensation on account of the variable activity of the functional groups of the monomers [79].

The general principles of calculation of the kinetics and statistic characteristics of reaction products, as developed by the author in the preparation and modification of polymers, make it possible to take a scientific approach to specific industrial processes on account of the specifics related to the polymeric nature of reactants [79].

The important investigaitons of non-equilibrium copolycondensation and polycondensation of monomers of asymmetric structure ("head-tail") were carried out by S.V. Vinogradova and V.A. Vasnov [76, 80]. As a result of their works, in 1972 the basic common tendencies of the formation of macromolecules of mixed polymers were formulated in the case of non-equilibrium polycondensation in the homogeneous system. More particularly, it was found that in order to form block copolymers under non-equilibrium copolycondensation conditions, comonomers showing different activities should be used. Besides, the rate of addition of the intermonomer into the reaction zone should be lower than the rate of its interaction with a more active comonomer. The experimental data on the effect of various factors on the composition and structure of copolymers were supported by the basic conclusions of quantitative theory of non-equilibrium copolymerization in the homogeneous system [80].

The works of the last years on polycondensation showed the limiting nature of the principle of equal reactivity of the functional groups (Flory's principle). This principle served as a cornerstone

of the entire theoretical research and methods for processing experimental data. Using acceptor-catalytic polycondensation, it was found that the activity of the terminal groups of polymer chains depends appreciably on the degree of polymerization, the nature of this dependence being determined by the structure of macromolecules and by the nature of the solvent used [81].

3.3. Polycyclocondensation

Polycyclocondensation of methylaryl ketones or their ketals leading to the formation of polymers of the polyphenylene type represents an interesting variety of polycondensation processes [82]. The basic common tendencies of this process were found [83, 84].

It should be noted that basic research of Soviet scientists into polycondensation has led not only to the creation of the theory of polycondensation processes, but to some techniques for manufacturing polymeric materials.

4. REACTIONS OF POLYMERS

The investigations of various reactions of macromolecules were begun as far back as the last century when nitration of cellulose and vulcanization of sulphur with rubber were performed for the first time. However, only in this century the chemists' works came to completion in this trend, thus making it possible not only to modernize production substantially, but also to obtain new interesting materials.

The investigations of the reactions of polymers are due, first of all, to P.P. Shorygin who, as far back as the 1920s, carried out basic research into the chemistry of carbohydrates [85]. A big contribution to this field was made by Z.A. Rogovin. During the postwar years S.N. Ushakov began working intensively on theoretical problems relating to polymeranalogous transformations, the interaction between macromolecules, and polycyclization, more particularly reactions in the preparation of graft high molecular weight compounds [86].

In the 1960s and 1970s, considerable progress was made in the development of a general theory on the reactivity of macromolecules. In their works N.A. Plate and his co-workers suggested a quantitative approach to the description of macromolecular reactions, thus making it possible to calculate the parameters of unit distribution and composition heterogeneity of polymeranalogous reaction products. A special mathematical device was devised to describe the structure of such products. The operation of the device was based on accurate and approximate methods including Mar-

kov's approximations and the Monte Carlo mathematical modelling method. Besides, the authors proposed a method of polymer models for determining individual rate constants of specific macromolecular reactions from kinetic data [87, 88].

The presence of theoretical fundamentals and the use of new kinetic and structural investigation methods permit establishing the mechanism of many practically important macromolecular reactions, to predict the product structure and its chemical and physicomechanical properties and to find methods for oriented synthesis of practically valuable polymeric materials having the predetermined properties.

Specific ionic polyreactions, including matrix ones, which model some important features of biosynthesis, were carried out for the first time by V.A. Kabanov and his co-workers [89]. The principle of matrix chain growth was also applied to conventional radical processes; the phenomena of "recognizing" complementary matrices by growing polymer chains were explained; a number of highly effective polymeric catalysts and reagents modelling enzymes were synthesized and studied [90, 91]. The investigations of cooperative interaction between synthetic complementary macromolecules laid the theoretical fundamentals of the chemistry and physical chemistry of cooperative polymer-polymer compounds [92]. The new type of substitution reactions was found in compounds in which the whole macromolecules act as substituting fragments, and the general principle of the self-composing of ordered structures from chemically complementary linear and globular macromolecules were established; and morphological analogues of nucleoprotein complexes were prepared [93].

In recent years, A.P. Suprun and his co-workers have shown that there is every possibility of obtaining heterogeneous macromolecules chemically bonded along the chain as chlorine-containing and aromatic polymers interact under Friedel-Crafts reaction conditions [94]. Such a trend in the synthesis of modified polymers opens wide possibilities of varying their properties as desired.

Solid-phase polycyclization leading to the formation of heat-resistant polyheteroarylenes is of particular interest among polymer reactions. V.V. Korshak, M.M. Koton, A.N. Pravednikov, and their co-workers devoted much attention to this problem.

Using reactions for the formation of 1,3,4-polyoxadiazoles as an example, V.V. Korshak, G.L. Berestneva, and their co-workers have shown that the specific features of polycyclization are caused by the occurrence of the process in the solid phase and by the intramolecular nature of cycle formation [95]. Owing to this fact thermal polycyclization reactions are structurally sensitive. The degree of cyclization and the rate of cycle formation are substantially dependent on factors such as the stereochemistry of functional

groups in the reaction fragment of the unit, the possibility of conformation transformations in the chains, the nature and degree of mutual ordering of macromolecules of the initial polymer, and the variation of this ordering in the course of the reaction.

The investigation of the kinetics of polycyclization of prepolymers into polyheteroarylenes has enabled A.N. Pravednikov and his co-workers to establish that the process rate is determined by the reactivity of the functional groups and the flexibility of the polymer chains [96, 97]. A lower flexibility of macromolecules in the formation of heterocycles leads to a sharp decrease in the reaction rate.

Recently, A.N. Pravednikov, E.N. Teleshov, and their co-workers have developed a new method for synthesizing polyheteroarylenes, i.e. isomerization cyclization [98, 99]. Nitrile-containing prepolymers of various types are transformed by this method into the end structures without liberation of volatile products; this presents a great practical interest. The investigation of isomerization cyclization of polycyanamides and polycyanureas showed that this process is accelerated with bases and proceeds according to the mechanism of general base catalysis.

5. DESTRUCTION AND STABILIZATION OF POLYMERS

The basic research carried out by N.N. Semenov into chemical chain reactions followed by the research carried out by N.M. Emanuel, V.V. Voevodsky, V.N. Kondratiev, M.B. Neiman, A.B. Nalbandyan, and A.A. Kovalsky laid a solid foundation for the solution of the problems of destruction and stabilization of polymers.

The wide application of theoretical and experimental methods of chemical physics has enabled N.M. Emanuel and his school to obtain and generalize data on the kinetics and the mechanism of polymer ageing. By looking at the kinetics of the way the important properties of polymeric materials vary and the mechanisms of those processes, methods for evaluating and improving their service life could be developed. New approaches to the stabilization of polymeric materials and to their utilization have been suggested.

In the investigation of destruction of polymers in liquid and gas aggressive substances, G.E. Zaikov and his co-workers have developed a theory of polymer destruction induced by solutions of aggressive substances which diffuse into the polymer. The authors also obtained theoretical dependences that allow solving the problems of prediction of variation in the weight, mechanical properties of polymeric articles to be found in an aggressive medium, duration of the protective action of polymeric coatings, and the

like [101-103]. The authors have proposed methods for modifying polymeric materials by subjecting them to controlled action of some aggressive substances.

G.E. Zaikov, A.A. Popov, and other researchers have begun investigating the problem of influence of the tensile stress on the kinetics of polymer reactions. It has been established that in the presence of load that varies the geometry of the reaction centre, the chemical process may be either accelerated or retarded [104]. For example, in the reaction of addition of ozone by the double bond, the tensile stress reduces the activity of *cis*-C=C-bonds, increases the reactivity of *trans*-C=C-bonds and exerts no influence on the activity of double bonds in the side chain [105]. A quantitative dependence was obtained for the reaction of abstraction of the hydrogen atom from the stretched carbon chain. This dependence correlates the reaction rate and the value of tensile stress applied [104, 106].

D.Ya. Toptygin has established the nature of macroradicals whose formation promotes the destruction of polyamides, polycarbonate, and polymethylmethacrylate. He has studied thermal and photochemical transformations of these radicals (more particularly, those leading to macromolecular rupture) and also the regularities of variations in the durability of polymers when both mechanical loads are applied and free radicals are involved simultaneously [107-109].

A.L. Buchachenko and his co-workers have made a considerable contribution to elucidating the kinetic regularities of radical reactions in a solid polymer in the course of polymer ageing [110]. The results obtained are of great importance in solving the problem of predicting the service life of polymeric articles.

As a result of the study of photooxidation of polymers V.Ya. Shlyapintokh and his co-workers showed that the widely spread conceptions on a great role of singlet oxygen in these reactions are erroneous. The authors obtained quantitative characteristics that permitted calculating the absolute rate of photooxidation of solid polypropylene and revealed the mechanism of action of a number of effective light stabilizers of polyamides [111, 112].

The appearance of new polymers that are highly resistant to high temperatures has led to the expansion of temperature ranges in the investigation of the processes of polymer oxidation.

The investigation of the kinetics of high-temperature oxidation of polymers enabled Yu.A. Shlyapnikov and his co-workers to establish that the autocatalytic nature of the reaction is due to the accumulation of aldehyde, rather than hydroperoxide groups. "Aldehyde branching" was known earlier for reactions in the gas phase [113].

To stabilize polymers, G.P. Gladyshev and his co-workers pro-

posed a method according to which salts of variable valence metals are introduced into the polymer. These salts undergo transformations under high temperatures which lead to considerable stabilization of polymers [114].

As a result of the investigation of the mechanism of action of antioxidants and light stabilizers, new thermal and light stabilizers were obtained, part of which are used for industrial purposes [115, 116].

G.A. Razuvaev, K.S. Minsker, B.B. Troitsky, and V.S. Pudov have made a considerable contribution to elucidating the kinetic regularities and the mechanism of destruction of polyvinyl chloride [117-119], thus making it possible to improve stability of this polymer which is important in practical aspects.

In the 1960s, an intensive investigation of the processes for the decomposition of heat-resistant polycondensation polymers of various classes was begun.

S.R. Rafikov, S.A. Pavlova, and their co-workers have studied the kinetics and the mechanism of thermal, thermooxidative, hydrolytical, and radiation ageing of heterochain polymers [120]. It was found that ageing processes are characterized by destruction (according to the homo- and heterolytical mechanisms) and structurization which occur simultaneously to form branched, cross-linked, and highly condensed structures. As a result of these investigations the authors have developed a new process for the stabilization of heat-resistant polymers by introduction into the polymer system of compounds capable of being decomposed at high temperatures to form active terminators of radical-chain processes.

In recent years, as a result of the investigation of chemical transformations of polymers at elevated temperatures, S.A. Pavlova and her co-workers have revealed the role of various factors of the chemical structure of polymer macromolecules and the nature of the mechanism of destruction at different temperature ranges [121-123]. The authors have established that *o*- and *m*-carboranes and their derivatives vary appreciably the direction of chemical transformations of polymers and may be used as stabilizers [124].

The research carried out by A.N. Pravednikov, O.G. Tarakanov, and their co-workers has shown an important role of radical-chain processes in the case of thermal destruction of polycarbonates, polysulphones, and polyurethanes [125-127].

G.L. Slonimsky and A.A. Askadsky have developed a calculation method for evaluating temperatures of intensive thermal destruction of polymers. This method is based on the analysis of the unit structure and terminal groups in the macromolecules [128, 129].

The works of A.A. Berlin, V.E. Gul', and N.K. Baramboim on the mechanochemistry and cryochemistry of polymers are of great scientific and practical importance. The establishment of

the mechanism of transformation of polymers in the course of their processing and service life made it possible to prepare polymeric materials having the combination of desired properties [130-132].

Owing to solving the problems of destruction of polymers and the choice of stabilizers, the boundaries for practical utilization of polymeric articles have been considerably broadened, their quality improved, and service life prolonged; this produces a great economic effect.

6. BASIC TYPES OF POLYMERS

At present, a great number of various polymers have been produced in the USSR. Some practically valuable high molecular weight compounds have been synthesized for the first time. Advancements in this field arise mainly from the results of profound research into the processes of synthesis and structure of high molecular weight compounds and close interrelationship between science and industry.

The investigation of the regularities and the mechanism of formation of heterochain polymers and the influence of the chemical structure on the properties of polyheteroarylenes has led V.V. Korshak and his school to establish the basic principles of polymer chain building and synthesis conditions and to create a new type of thermostable soluble linear polymers—cardo polymers (polyarylates, polyamides, polyimides, polyoxadiazoles, and the like) having valuable properties [133]. The research of many years into the regularities of polycondensation and properties of heterochain polymers allowed laying scientific fundamentals of the synthesis of block copolymers of the polycondensation type, more particularly, multicomponent block copolymers having the predetermined properties [80, 134].

The results of the investigation of the effect of the nature of activators on the process of anionic polymerization, obtained by T.M. Frunze and his co-workers, permitted synthesizing copolymers of different structure including graft and block copolymers having a wide range of physicomechanical properties [135].

A comprehensive investigation of the structure and physicochemical properties of comb-like polymers enabled N.A. Plate, V.P. Shibaev, and their co-workers to reveal their peculiar features and formulate the basic principles forming the foundation for the behaviour of these polymers in various physical and phase states [23].

Of great importance are the works of K.A. Andrianov, N.S. Enikolopov, A.A. Zhdanov, E.F. Oleinik, and their co-workers on oriented synthesis and filling of cross-linked polymers.

In the mid 70s, V.V. Korshak put forward the principle of the raznozvennost' (different-unit structure) of polymers. According

to this principle, in the course of synthesis macromolecules containing abnormal units are formed from side processes [136]. In view of this fact one of the major problems of synthetic chemistry is revealing possibilities of controlling the number of abnormal units and their distribution along the chain.

The basic high molecular weight compounds that are successfully developed in the USSR include polyhydrocarbons; phenol-formaldehyde, carbamide and epoxy polymers; polyethers and polyesters; polyamides, polyurethanes, polyheteroarylenes, organoelement polymers, cellulose, and some other compounds.

6.1. Polyhydrocarbons and Their Derivatives

Great progress has been made in the USSR in the preparation of synthetic rubber. From the very outset in the mid 19th century, the world rubber industry was oriented exclusively on cheap and high-quality natural rubber produced in abundance, although work had been under way on the synthesis of rubber-like polymers by the beginning of the 20th century.

Trade restrictions of the suppliers of natural rubber forced the young Soviet Republic in its early period of existense to solve the problem of synthetic rubber. The synthesis of rubber from diene hydrocarbons was made possible in 1901-1914 in the works of I.L. Kondakov, L.M. Kucherov, and S.V. Lebedev. However, rubber could be synthesized only after Lebedev developed a method of catalytic transformation of ethanol into butadiene with high technical-and-economic indices. This method was employed at the plants producing synthetic butadiene rubber constructed in the USSR in 1931.

In the 1930s, A.E. Favorsky synthesized isoprene based on acetone and acetylene and developed an industrial method for the preparation of isoprene rubber, and he won the State prize in 1941. The reaction which laid the foundation for the preparation of isoprene permitted Favorsky to synthesize some other monomers.

A valuable contribution to the expansion of a variety of monomers for rubber synthesis was made by N.D. Zelinsky and A.A. Balandin. They were awarded the S.V. Lebedev prize in 1946 for their research work on the production of unsaturated hydrocarbons by the catalytic dehydrogenation method.

The reaction of catalytic hydropolymerization of acetylene is of particular theoretical and practical interest. This reaction was discovered by A.D. Petrov in 1942 at the Institute of Organic Chemistry and allowed preparation of isobutylene with a yield of up to 95%. The author won the State prize and the S.V. Lebedev prize for his research work in 1947.

The dehydrogenation of pentanes and pentenes into isoprene was effected on an industrial scale in the 1950s, and was based on the works of N.I. Shuikin, Yu.G. Mamedaliev, A.A. Balandin and their co-workers. During that period, studies of rubber synthesis, which are traditional for the chemistry of high molecular weight compounds in the USSR, took a different direction. The problem of monomers was no longer acute and it was replaced by a more profound investigation of the polymerization of diene hydrocarbons where the properties of rubber depend on the rubber preparation method.

The investigations of stereospecific polymerization of diene hydrocarbons have enabled A.A. Korotkov and his co-workers to synthesize rubber of the SKI type which is essentially *cis*-1,4-polyisoprene, and allowed B.A. Dolgoplosk and his co-workers to prepare *cis*-1,4-polybutadiene (synthetic rubber of the SKD type). Putting these high-quality synthetic rubbers to industrial uses has pushed the rubber industry to an essentially higher level. Korotkov and his co-workers won the Lenin prize in 1967 for developing and putting to industrial uses SKI-type rubber, and Dolgoplosk was awarded the S.V. Lebedev prize in 1962 for proposing a technological method for the production of synthetic SKD-type rubber.

As to the technical level and assortment of general-purpose synthetic rubbers the USSR now leads the world. As to the scale of production, stereoregular rubbers (*cis*-polyisoprene and *cis*-polybutadiene) are now the main types of general-purpose rubbers.

G.A. Dolgoplosk and his co-workers have developed original catalytic systems based on organometallic compounds of transition metals which allow preparing *cis*- and *trans*-polymers and copolymers of dienes, polypiperilene, atactic and syndiotactic (crystalline) 1,2-polybutadiene, and also systems for the preparation of *cis*-copolymers of butadiene with isoprene, which present interest as general-purpose high-elastic rubbers [36-38].

A problem of the synthesis of oligomers (liquid rubbers) containing terminal functional groups capable of being transformed into linear or cross-linked structures has been solved to advantage [137].

A considerable contribution to the development of theoretical foundations and the technology of rubber vulcanization was made by B.A. Dogadkin and I.A. Tutorsky [138]. The works of A.I. Dolgopol'sky, A.L. Klebansky, V.L. Karpov, and Yu.S. Zuev contributed to developing the chemistry of rubbers and rubber products.

It is very interesting to trace how polyolefins developed in the USSR. G.G. Gustavson obtained polyethylene in 1884 by the polymerization of ethylene in the presence of aluminium bromide; however, its molecular weight was low. As late as 1933-1936, the Soviet and British researchers managed to prepare high molecular

weight polyethylene by the polymerization of ethylene at high pressures and elevated temperatures [139].

After K. Ziegler discovered complex organometallic catalysts in the 1950s, the development of a new process for preparing polyethylene at low pressure was started in the USSR. The works of V.A. Kargin, A.V. Topchiev, S.N. Ushakov, V.A. Kabanov, B.A. Krentsel, and their co-workers at the Leningrad Research and Design Institute of Polymerization Plastics made a great contribution to this research; appreciable advances have been made in the field of polyolefins, polystyrene and vinyl acetate plastics, and fluorine-containing polymers.

It will be noted that a combination of valuable properties of polyolefins determines their leading place in output and consumption among polymerization plastics. The creation of highly efficient processes was the typical feature in the 1970s for the polymerization polymer industry. In this connection, the process for preparing low-density polyethylene in tubular reactors (Polimir-50), jointly developed by Soviet and GDR scientists, has been a major achievement of Soviet science and industry.

Polyvinyl chloride was of particular interest among halogen-containing polyolefins. I.I. Ostromyslensky synthesized polyvinyl chloride from vinyl chloride in 1918. Some time later I.P. Losev, B.N. Rutovsky, G.M. Pavlovich, and other researchers studied the synthesis of polyvinyl chloride. As a result, industrial processes for preparing appropriate plastics based on chlorine-containing monomers, such as vinyl chloride and vinylidene chloride, were created. Major theoretical and practical research into polyvinyl chloride and polyvinyl chloride-base compositions, and also into various polyacrylates was carried out in the 1970s at the V.A. Kargin All-Union Research Institute of the Chemistry and Technology of Polymers.

The research work on the synthesis of fluorine derivatives of polyolefins was started in the 1940s in the USSR. The production of polytetrafluoroethylene (fluoroplast-4) was started in 1949. Fluoroplast-4 has various applications owing to its unique properties.

The development of methods of synthesis of vinyl ethers, vinyl acetate, and other vinyl-containing monomers allowed industrial preparation of polymers based on these compounds. A great contribution in this work was made by A.E. Favorsky. In collaboration with I.N. Nazarov he created a new perspective method for synthesizing vinylethynyl carbinols [140]. Nazarov used polymerization of dimethylvinylethynyl carbinol to obtain carbinol adhesives which found wide industrial applications, for which research Nazarov was awarded the State prize in 1942. In 1946 he won the State prize for his basic research into acetylene and its derivatives.

In 1939 A.E. Favorsky and M.F. Shostakovsky proposed a simple process for synthesizing vinyl ethers which were used in the preparation of some polymers [141]. Shostakovsky was awarded the State prize for his research on the development and industrial application of a method for the preparation of vinyl ethers.

Systematic studies of the polymerization of vinyl esters were undertaken by S.N. Ushakov who developed suitable methods for synthesizing polyvinyl acetate, polyvinyl alcohol, and its various derivatives [86].

The research work on the synthesis of acrylic polymers was done on an extensive scale in the 1950s in the USSR. As a result, industrial processes for the preparation of widely used acrylic polymers and copolymers were created.

A.M. Polyakova and her co-workers undertook a series of investigations to prepare adhesives for various branches of engineering, and for seamless joints in the living organism tissues as applied in medicine. These adhesives are based on monomeric ethers of α-cyanacrylic acid [142, 143].

New processes for synthesizing polyphenylenes, namely polycyclopolymerization and polycyclocondensation were created. Materials and compositions based on oligophenylenes can be serviceable for long periods at elevated temperatures. Means for the modifications of polyphenylenes were devised with a view to improving the technological parameters of their structurization [144, 145].

Of tremendous interest was a new linear form of carbon, i.e. carbin, obtained by V.V. Korshak and A.M. Sladkov in 1961 by the dehydropolycondensation of acetylene [146].

6.2. Phenolformaldehyde Polymers

The work on the creation of phenolformaldehyde polymers is attributed to G.S. Petrov. The production of phenolformaldehyde polymers was started at the plant in Orekhovo-Zuevo in 1914 and at the Okhtinsk chemical plant in 1928. Accessibility of the raw material base, processibility of the synthesis process, superior mechanical, dielectric and anticorrosive properties of phenolformaldehyde polymers allowed their wide applications.

A group of research workers at the Leningrad Chemical Technological Institute headed by A.A. Vansheidt carried out interesting studies into the synthesis of phenolformaldehyde polymers, and G.S. Petrov, I.P. Losev, and other researchers carried out research on their modification.

Studies of phenolformaldehyde polymers were carried out in the 1970s basically in the two trends: creation of new types of polymers and polymer-base materials and the investigation of a process for the formation of oligomers.

V. A. Sergeev, G. Sh. Papava, and other research workers proposed processes for preparing new phenolformaldehyde polymers based on phenolphthalein and phenol (СФ-490) and bisphenols of the norbornane type [147, 148]. At present, polymer СФ-490 is used to advantage as a binder for glass-reinforced plastics which can be serviceable at elevated temperatures. These glass-reinforced plastics are twice as strong as glass-reinforced plastics based on conventional phenolformaldehyde polymers.

Studies of the isomerism in the series of the phenol- and resorcinolformaldehyde oligomers allowed establishing the interrelation between the conditions of synthesis of oligomers, their isomeric compositions, and curing rate. The results obtained were used to create quickly-curable phenolic polymers [149].

6.3. Epoxy Polymers

Intensive investigations of the synthesis of epoxy polymers were undertaken in the USSR after the Second World War. Valuable technological, physicomechanical, and dielectric properties of epoxy polymers allowed their wide application in the manufacture of glass-reinforced plastics, pressing and moulding compositions, adhesives and paint coatings. Work is being done on the synthesis of new types of epoxy polymers and epoxy polymer-base compositions, the mechanism of their formation, methods for curing and filling epoxy polymers and their reactions with various curing agents.

In recent years N.S. Enikolopov, E.F. Oleinik, and other researchers have obtained new results on the correlation between the structure of cross-linked epoxy polymers and their mechanical and thermal properties; they have also obtained new data on the influence of the oligomer curing process on the physical properties of cross-linked systems [150, 151]. It was found that after completion of the curing reaction, the heat stability of the resulting polymer can be determined by its curing temperature, or in other words, it is impossible to prepare thermally stable polymers at low curing temperatures. The results of investigations of the kinetics and mechanism of curing epoxy resins affected by various curing agents enabled the researchers to determine kinetic and thermodynamic parameters of the process and to approach the problems of utilization of catalysts and curing agents.

6.4. Polyethers and Their Sulphur-containing Analogues

A.A. Petrov, A.A. Berlin, A.V. Topchiev, B.A. Krentsel, and other scientists began to tackle the problem of synthesis of polyethers in the 1940s. They studied the mechanism of a poly-

merization reaction of α-oxides and means for improving its efficiency by various catalytic systems [152].

M.G. Gonikberg managed to prepare oxygen-containing polymers by the polymerization of aldehydes in the 1950s [153]. Later on the main attention was paid to the investigation of formaldehyde polymerization. At present, the national economy widely employs polyformaldehyde, pentaplastic, aromatic polyethers, and the like. The research work done at the Moscow Science and Production Association "Plastmassy" and at the Leningrad Science and Production Association "Plastpolimer" makes a considerable contribution in this respect. These associations helped to start industrial and pilot production.

In the 1970s, V.A. Ponomarenko carried out the synthesis of some new fluorine-containing heterochain polymers [154].

In the 1970s, considerable progress was made to prepare aromatic polyethers and polythioethers.

Polyarylene sulphides developed by V.A. Sergeev and his co-workers appear to be the most promising representatives of this type of polymers [155]. New processes were created for synthesizing poly- and oligoarylene sulphides capable of being cross-linked in the course of chemical transformations. Higher thermo- and heat-resistant polysulphones of the appropriate structure were obtained by oxidation of oligo- and polyarylene sulphides. Thermosetting amino- and maleinimido-containing polyarylene sulphides having improved fire resistance properties were derived from modified sulphur-containing polyarylenes with halogen atoms in the chain [156]. Processes for synthesizing low-melting and soluble polyarylene sulphides were developed, thus making it possible to process them readily into articles [157].

Polyesters occupy the leading position: their production was started more than 50 years ago. Investigation of polyesters such as alkyd, which are referred to the group of synthetic varnish and paint materials, was started in the 1920s, and that of unsaturated polyesters and polyethylene terephthalate in the 1930s. The research in the above-mentioned trends was carried out by B.V. Maksorov, K.A. Andrianov, G.S. Petrov, S.N. Ushakov, M.M. Koton, A.A. Berlin, and other scientists. In 1947 V.V. Korshak and his co-workers began synthesizing polyethylene terephthalate on the basis of which "lavsan" fibre was manufactured [158].

Thermally stable polyesters, polyarylates, were synthesized in the 1950s at the Institute of Organoelement Compounds of the USSR Academy of Sciences. They are used in instrument making, in the manufacture of filter media, antifriction self-lubricating plastics, and the like.

The 1960s and 1970s saw the advances in the synthesis of cardo and conformationally regular polyarylates, the use of oligoarylate

blocks in the preparation of multicomponent block copolymers, and the like [76, 120, 133, 134].

In the 1970s, M.F. Sorokin and his co-workers proposed a process for preparing alkyd and unsaturated polyesters using epoxy derivatives of dicyclopentadiene. The latter is the waste of the coke industry and oil refining [159]. Oligoester acrylates and oligoester acrylate-base materials were put to industrial uses owing to A.A. Berlin's works [160].

The Moscow Science and Production Association "Plastmassy" carries out research aimed at creating new thermoplastic structural materials such as polycarbonates and polyalkylene terephthalates.

6.5. Carbamide Polymers, Polyamides, and Polyurethanes

Carbamide polymers began to be manufactured by the Soviet industry by the late 20s. Cheap raw materials and simple technology in the synthesis of carbamide polymers during the prewar period brought about their wide applications [161].

Polyamide synthesis was started during the Great Patriotic War; the fundamental works of V.V. Korshak, S.R. Rafikov, I.P. Losev, and their co-workers were devoted to it [162].

The works of I.L. Knunyants, Z.A. Rogovin, and other researchers in the production of polycaproamide and "capron" are widely known. I.L. Knunyants carried out interesting investigations to prepare aromatic fluorine-containing polyamides [163].

From the 1960s, intensive studies of new polyamides, such as caprolite and phenylon, have been undertaken in the USSR. Various types of activators were found to affect the properties of caprolite which is superior to capron in physicomechanical properties [43, 44]. Phenylon (poly-*m*-phenylene-isophthalamide) possesses extremely valuable properties. Important studies of this polyamide were carried out by L.B. Sokolov [78]. Phenylon-base plastic is used in the electrical and machine-building industries, and in other branches.

In the 1970s, the Moscow Science and Production Association "Plastmassy" created a wide variety of carbamide polymers, urea- and melamino-formaldehyde moulding materials, and developed continuous technological processes for the production of multiton articles, which had been mastered on an industrial scale.

Studies of the catalysis mechanism of reactions of polyurethane formation enabled Yu.S. Lipatov and his co-workers to establish correlation between the structure of the catalyst and its activity [164]. As a result of the investigation of the kinetics and properties of macromolecules at different stages of polymer network formation, T.E. Lipatova created a theory of structural gel formation. This theory permitted establishing peculiar features of the chemical

behaviour of polyurethanes (polyurethane enamels, adhesives, thermoplastic materials, surgery materials, and the like) which found wide practical applications [165].

6.6. Heterocyclochain Polymers

Polymers containing five- and six-member heterocycles bonded by single bonds or condensed with other cycles relate to high molecular weight compounds with improved heat resistance and thermostability [166]. The aforementioned polymers could be prepared due to the works of V.V. Korshak, M.M. Koton, A.N. Pravednikov, S.V. Vinogradova, A.A. Berlin, B.A. Zhubanov, S.R. Rafikov, and other researchers.

Comprehensive research is being done by M.M. Koton, S.V. Vinogradova, and other scientists on the synthesis and study of the properties of polyimides, more particularly aromatic polyimides [133, 167 - 170]. Owing to a combination of rigid cycle macromolecular fragments containing "hinged" oxygen and sulphur atoms, or other groups, and also thanks to the variation of their number and disposition in the chain, polyimides were synthesized that have a wide spectrum of properties—from elastic to very rigid ones. The works on the catalytic reaction of dianhydrides with diamines promoted the preparation of these polyimides [170]. The use of carboxylic acids in polyimide formation does not only ensure milder conditions, but allows synthesis of high molecular weight polynaphthoyleneimides, which are superior in hydrolytic stability and heat resistance over currently used polypyromellitimides.

The isomeric raznozvennost' (different-unit structure) of polyamido acid macromolecules was for the first time discovered and determined by the method of NMR spectroscopy [171, 172].

Thermally stable polyheteroarylenes containing imide cycles in the macromolecules appear to be promising in the manufacture of films, fibres, coatings, composition materials with good mechanical properties within wide temperature ranges.

The search for the structures of prepolymers whose cyclization could proceed without liberation of volatile products attempted by A.N. Pravednikov in the 1970s, led him to develop an isomerization method for polyheteroarylene synthesis based on interaction of amide or urea groups in the prepolymers with nitrile groups [99, 173]. This method was first used in the preparation of polybenzimidazo-, polyquinazolono-, and polyiminoquinazolonopyrrolones. These polymers have high heat resistance and, in some cases, show good physicomechanical properties.

As a result of the investigation of polybenzoxazoles, polybenzimidazoles, polyoxadiazoles, polyisoindole quinazolindiones, polyphenylquinoxalines, and other high molecular weight heterocyclic com-

pounds carried out by V.V. Korshak and his school, the correlation has been established between the chemical structure of polymers and their thermal characteristics [166, 174 - 176]. Some of the synthesized heterocyclochain polymers are of particular interest, e.g. polyphenylquinoxalines, which show high thermal and chemical stability, solubility, and good processibility. In the synthesis of ladder polyheteroarylenes, which are known to have a high degree of cyclization and are superior in heat resistance and thermostability to conventional polyheteroarylenes, three-step polycycloconden-sation of aromatic tetrafunctional nucleophiles, more particularly bis(*o*-phenylenediamines) and bisamidrazones of dicarboxylic acids with aromatic tetracarboxylic acids and their derivatives, attracts the utmost attention [177]. Two-step polycyclocondensation of aromatic dicarboxylic acid derivatives with aromatic diamines containing nitrogen heterocycles with labile hydrogen atoms in the *ortho* position with respect to the amino group has also been elaborated. Polybenzo-bis(pyrimidobenzimidazoles), which occupy the intermediate position between polyheteroarylenes and graphite, possess the highest thermostability in the series of the ladder polymers obtained [174].

V.V. Korshak and A.L. Rusanov have developed a new method for synthesis of polyheteroarylenes, i.e. reducing polyheterocyclization. Phenylated polyheteroarylenes were prepared by this method. They are characterized by both high heat resistance and improved processibility into articles [178].

S. V. Vinogradova and V. A. Pankratov have laid scientific foundations for the synthesis of new regularly cross-linked thermosetting polymers by polycyclotrimerization of monomers with C—N multiple bonds [54, 179]. The researchers carried out synthesis and studied the properties of thermally stable polymers on the basis of di- and polyfunctional aromatic and organoelement cyano esters, isocyanates, cyanamides, nitriles, carbodiimides and their copolymers with different monomers. Most of the initial monomers are multiton industrial products (isocyanates or carbodiimides) or may be prepared by a simple method from available raw materials (dicyanates, cyanamides, or nitriles). They carried out a comprehensive investigation of the physical properties of the resulting cross-linked systems and revealed specific features of this class polymers. These features are caused by the regular nature of the polymer structure. For example, the researchers found that the series of polycyanurates and polyisocyanurates based on aromatic and organoelement dicyanates and diisocyanates possess high physicomechanical properties. They are much superior in this respect to most known cross-linked rigid-chain polymers. Some polycyanurates and polymelamines have a partially crystalline structure. Most of the resulting cross-linked polymers were found to have valuable properties.

The results of the research into polyheteroarylenes were further improved as industrial technology was developed at the Science and Production Association "Plastmassy" for the preparation of polyheteroarylenes. A.Ya. Chernikhov and his co-workers have created a number of "niplon" materials based on the polyheteroarylene series which show high physical properties under thermal, thermooxidative, radiation, and chemical conditions [180]. In particular, in order to create new high-efficient ultrafilters, coatings and injection-moulded materials, cardo polyoxadiazoles were used. Molding materials for structural purposes were created on the basis of polybenzoxazoles. The researchers used the principle of isomerization cyclization to develop a new type of valuable thermosetting plastics [181]. Both the reaction for the formation of thermostable polymers and the process for the manufacture of articles have found wide practical applications in the preparation of new types of pasty glues and binding agents for abrasive tools.

6.7. Organoelement Polymers

The chemistry of organoelement compounds founded in the USSR by A.N. Nesmeyanov laid the basis for the development of chemistry of various organoelement polymers.

In 1937 K.A. Andrianov managed to show that polymer chains may be built up from alternating silicon and oxygen atoms [182]. He formulated and put into practice the principle of a combination of elements of different electronegativity in the polymer chain. In subsequent years, in addition to the studies of classical structures of organosilicon polymers (both linear and branched), nontraditional and specific structures of polymer molecules (such as cyclonetwork, cyclolinear, ladder, spirocyclic, and the like) were investigated. This allowed synthesis of different organosilicon polymers to be effected on an industrial scale in 1944-1947.

Linear and branched oligomers were synthesized by K.A. Andrianov and his school in the 1950s-1970s. As a result of polymerization and polycondensation, these oligomers can be transformed into high molecular weight compounds with properties useful in practical terms; polymerization and polycondensation processes may be carried out directly in the course of molding articles [183, 184]. In particular, polycondensation of such oligomers produces polymers of ordered network structure, whose capacity to crystallization depends on the length between the cross-linking points, or soluble spirocyclic polymers [185].

N.S. Nametkin in the 1960s created a new class of polysiliconhydrocarbons which found practical applications. In particular, polyvinyltrimethyl silane proved to be quite a promising material in the preparation of highly efficient gas separation membranes [186].

In the 1970s, the researchers' attention was directed to organosilicon compounds containing Si—N bonds, more particularly to the common tendencies in the formation of this bond in organoaminosilanes and organosilazanes [187]. D.Ya. Zhinkin and M.V. Sobolevsky elaborated the technology for manufacturing individual organosilazanes and copolymers of the silazane structure [188]. Since polyorganosilazanes undergo almost complete transformation into polyorganosiloxanes when contacted with air moisture, they are employed in the manufacture of cold drying protecting coatings as binder components, and for other purposes.

Organosilicon compounds containing aluminium and other metals developed by K.A. Andrianov and A.A. Zhdanov appear to be a promising group of organoelement polymers [189].

The discovery of a new class of organoboron compounds such as carboranes in 1962-1963 led to the creation of thermally stable organoelement carborane-containing polymers, in particular to those based on arylenecarboranes. The works of V.V. Korshak and his school dealt at length with the synthesis of initial monomers and carborane-containing high molecular weight compounds (e.g. polyarylates, polyamides, poly-1,3,4-oxadiazoles, and polyimides) [190, 191]. The studies of the properties of these polymers demonstrated that at elevated temperatures and in atmospheric air, they form thermostable three-dimensional cross-linked structures in which inorganic networks are found to be in combinations with three-dimensional organic macromolecules.

Synthesis of carborane-containing oligomers such as epoxides, phenolformaldehyde resols, oligophenylenes, and the like is one of the interesting trends in practical utilization of such polymers. When cured, they become interesting cross-linked structures [145].

In the 1970s, interesting results were obtained in the chemistry of polyphosphazenes. Some important regularities of thermal mass polymerization of hexachlorocyclotriphosphazene were established; this enabled the researchers to put forward a new conception on the mechanism of this process and to determine the methods for controlling the synthesis of polydichlorophosphazene [192, 193]. Carborane-containing polyphosphazenes possessing interesting properties were obtained by reaction of polymeranalogous transformations of polydichlorophosphazene with different carborane-containing nucleophiles [194].

6.8. Polymers with Special Properties

Great progress has been made in the preparation of polymers containing ionogenic groups, i.e. ionites and complexones (I.P. Losev, A.B. Davankov, K.M. Saldadze, G.V. Samsonov, V.A. Davankov, S.V. Rogozhin, and other researchers) [195-197].

In the 1970s, V.A. Davankov and his co-workers obtained a new class of three-dimensional polymers referred to as macroporous macronetwork structures. These polymers synthesized by cross-linking polystyrene chains with bifunctional reactants, according to the Friedel-Crafts reaction, have a highly cross-linked structure and a highly developed surface. They become swollen even in the media that cause polystyrene to precipitate from its solutions, including water and liquid nitrogen [198]. Organic substances are adequately absorbed by isoporous macronetwork structures from the gas phase, and from aqueous and organic media. Their capacity is substantially superior to that of sorbents of the conventional types and is combined nicely with the simplicity of regeneration. Thesé polymers may be regarded as a new type of non-specific sorbents. They are quite promising for protecting air and water basins against industrial waste [199].

Research was started in the 1960s and is being intensively carried out now by N.M. Emanuel, Z.A. Rogovin, N.A. Plate, N.S. Nametkin, G.V. Samsonov, A.S. Sadykov, and Kh.U. Usmanov on the use of polymers in medicine. This research is being done in the most various trends which cover, in particular, major branches of medicine such as surgery, creation of new and increasing the activity of the conventional drugs, and the like. Polymers intended for contact with blood and tissues of the living organism are being successfully employed in clinics as artificial blood vessels, heart valves, the artificial heart, semipermeable membranes for dialysis and oxygenation of blood, and so on [200, 201].

In recent years, interesting research was started by N.A. Kabanov and his co-workers on the use of polymers in immunology [202]. Immunogenes of a new type, namely polycomplexes (conjugates), were obtained by reacting proteins with polyelectrolytes. Immunization of mice by the methods of polycomplexes gives 50 to 100 times more antibody-forming cells as compared with pure protein solutions. Immunogenes containing linear polymer carriers present interest in the preparation of antiserums and antibodies by immunization of animals, and in the coming years, as artificial vaccination drugs.

Work was under way on the synthesis of liquid-crystalline polymers in the 1970s. N.A. Plate, S.P. Papkov, Yu.B. Amerik, V.P. Shibaev, V.G. Kul'chikhin, and other researchers established the basic principles of formation of mesomorphous polymeric systems which allowed synthesis of various thermal and lyotropic liquid-crystalline structures having interesting properties [22, 23, 203].

Great progress has been made for the last 20 years in the field of polymers containing a system of conjugated bonds. New polymers were synthesized and research was done to elucidate the conjugation mechanism. In their works, V.A. Kargin, B.A. Kren-

tsel, B.E. Davydov, A.A. Berlin, I.L. Kotlyarevsky, A.M. Sladkov, B.I. Liogon'ky, M.I. Cherkashin, Ya.M. Paushkin, and others dealt with the problems relating to the mechanism of poly conjugation of organic and organoelement polymers of different classes, the synthesis and mechanism of semi-conductivity of polymers containing conjugated bonds [204, 205].

6.9. Cellulose and Other Polysaccharides

The research carried out by Soviet scientists in the chemistry of cellulose and other polysaccharides occupies a special place in the chemistry of high molecular weight compounds. P.P. Shorygin was the first to do this research and he played an important role in creating the industry of artificial fibres. From 1924, P.P. Shorygin did a great deal of research into the chemistry of carbohydrates and set up a big school of prominent researchers who are developing successfully this trend.

Cellulose studies were made by outstanding Soviet chemists such as V.A. Kargin, N.I. Nikitin, S.N. Danilov, S.N. Ushakov, and Z.A. Rogovin. Cellulose is the most available and cheap polymer, and in order to improve efficiency of utilization of cellulose materials, valuable properties should be imparted to them and their perspective applications determined. As a result of systematic investigations, methods were developed for the introduction of reactive functional groups into the macromolecules of chemically modified cellulose; this allowed its further transformations. Besides, it was managed to synthesize new derivatives of cellulose and desoxycellulose and mixed polysaccharides containing such macromolecular units that are not to be found in natural polysaccharides [206]. The researchers established and formulated the basic principles of chemical transformations of cellulose and demonstrated the role of structural, stereochemical, and other factors.

In recent years, Z.A. Rogovin and his co-workers have obtained new classes of cellulose derivatives, i.e. phosphorus-, fluorine-, silicon-, mercury-, and tin-containing cellulose ethers and esters, desoxycellulose derivatives, and various graft copolymers. Systematic investigations of the regularities of synthesis of such cellulose copolymers, studies of their structure and properties enabled the researchers to develop the basis for industrial production of modified cellulose materials of new types [207].

From among polysaccharides dextran has been studied in detail in recent years. Dextran and its derivatives have found wide applications in medicine and biology. Various derivatives of this polysaccharide have been synthesized, dextran structural transformations studied in detail, graft copolymers and various structural modifications obtained, and conditions of their mutual conversions investigated.

7. CONCLUSION

The role of polymers in modern life is tremendous. One of the major problems of polymer science is concerned with creating new synthetic materials having the predetermined properties. The advances of the chemistry of high molecular weight compounds allowed preparation of quite a number of new materials that are essential in engineering, agriculture, construction, medicine, and in everyday life.

Major achievements have been attained in various branches of organic, organoelement and inorganic chemistry. Considerable progress has also been made in the development of fundamentals in the chemistry of high molecular weight compounds. The results of this research serve as a reliable guarantee of progress in science and engineering. Part of this research is presented in the given collection.

References

1. N.N. Semenov, *Chain Reactions*, Goskhimtekhizdat, Leningrad, 1934 (in Russian).
2. N.N. Semenov, *On Some Problems of Chemical Kinetics and Reactivity*, Izd. Akad. Nauk SSSR, Moscow, 1958 (in Russian).
3. S.S. Medvedev, O.M. Kozitskaya, and E.N. Alekseeva, *Zh. Fiz. Khimii*, 17, 391 (1943).
4. *Academician Sergei Vasil'yevich Lebedev, Life and Research*, ONTI, Khimteor., Leningrad, 1938 (in Russian).
5. V.V. Korshak, *General Methods of Synthesis of High Molecular Weight Compounds*, Izd. Akad. Nauk SSSR, 1953, vol. 1 (in Russian).
6. S.N. Kamenskaya and S.S. Medvedev, *Zh. Fiz. Khimii*, 14, 922 (1940).
7. Kh.S. Bagdasar'yan, *The Theory of Radical Polymerization*, Nauka, Moscow, 1966 (in Russian).
8. V.V. Korshak, *Izv. Akad. Nauk SSSR, OKhN*, No. 3, 269 (1949).
9. S.S. Medvedev, *Emulsion Polymerization*, in: *Kinetics and Mechanism of Formation and Transformation of Macromolecules*, Nauka, Moscow, 1968, p. 5 (in Russian).
10. V.A. Kabanov and D.A. Topchiev, *Radical Polymerization of Ionizable Monomers*, Nauka, Moscow, 1976 (in Russian).
11. V.P. Zubov and V.A. Kabanov, *Vysokomolek. Soed.*, 13A, 1305 (1971).
12. V.A. Kargin and V.A. Kabanov, *Zh. Vses. Khim. Ob-va im. D.I. Mendeleeva*, 9, 602 (1964).
13. A.I. Bol'shakov, A.M. Mikhailov, I.M. Barkalov, and V.I. Gol'dansky, *Dokl. Akad. Nauk SSSR*, 205, 379 (1972).
14. A.D. Abkin, P.M. Khomikovsky, E.V. Volkova, and V.I. Lukhovitsky, *Zh. Vses. Khim. Ob-va im. D.I. Mendeleeva*, 18, 246 (1973).
15. V.I. Gol'dansky, *Usp. Khimii*, 44, 2121 (1975).
16. S.S. Ivanchev, *Vysokomolek. Soed.*, 20A, 1923 (1978).
17. G.P. Gladyshev and S.R. Rafikov, *Usp. Khimii*, 35, 918, (1966).
18. S.I. Kuchanov, N.G. Ivanova, and S.S. Ivanchev, *Vysokomolek. Soed.*, 18A, 1870 (1976).
19. V.V. Korshak, N.V. Klimentova, A.P. Suprun, V.M. Zhukin, and M G. Golikberg, *Vysokomolek. Soed.*, 11A, 101 (1966).

20. I.I. Vointseva, A.P. Suprun, and T.A. Soboleva, *Vysokomolek. Soed.*, 16A, 998 (1974).
21. V.M. Zhulin, Z.G. Makarova, and N.V. Klimentova, *Vysokomolek. Soed.*, 23B, 724 (1981).
22. N.A. Plate and V.P. Shibaev, *Comb-shaped Polymers and Liquid Crystals*, Khimiya, Moscow, 1980 (in Russian).
23. Yu.B. Amerik and B.A. Krentsel, *The Chemistry of Liquid Crystals and Mesomorphous Polymer Systems*, Nauka, Moscow, 1981 (in Russian).
24. A.R. Gantmakher and S.S. Medvedev, *Zh. Fiz. Khimii*, 23, No. 5, 516-529 (1949).
25. *Academician Sergei Vasil'yevich Lebedev. On the 80th Birthday* (Eds. A.E. Arbuzov and S.R. Serienko), Izd. Akad. Nauk SSSR, Moscow, 1984 (in Russian).
26. S.S. Nametkin, *Research in the Fields of Organic Chemistry and Chemistry of Petroleum*, Nauka, Moscow, 1979 (in Russian).
27. A.V. Topchiev, *Polymerization. Organosilicon Compounds, Selected Proceed.*, Nauka, Moscow, 1966 (in Russian).
28. A.A. Korotkov, and A.F. Podol'sky, *Catalytic Polymerization of Vinyl Monomers*, Nauka, Leningrad, 1973, pp. 5-6 (in Russian).
29. Yu.A. Spirin, A.R. Gantmakher, and S.S. Medvedev, *Vysokomolek. Soed.*, 1, 1258 (1959).
30. A.A. Korotkov, N.N. Chesnokova, and L.B. Trukhmanova, *Vysokomolek. Soed.*, 1, 46 (1959).
31. A.V. Topchiev and B.A. Krentsel, *Usp. Khimii*, 25, 921 (1956).
32. *The Results of Science. Chemical Science. Chemistry and Technology of Synthetic High Molecular Weight Compounds. Carbochain Polymers* (Ed. V.V. Korshak), Nauka, Moscow, Issue 9, 1967 (in Russian).
33. E.I. Tinyakova, T.G. Zhuravlyova, T.N. Kurenogina, N.S. Kirikova, and B.A. Dolgoplosk, *Dokl. Akad. Nauk SSSR*, 144, 592 (1962).
34. A.V. Topchiev, B.A. Krentsel, N.F. Bogomolova, and Yu.Ya. Gol'dfarb, *Dokl. Akad. Nauk SSSR*, 111, 121 (1956).
35. V.A. Kargin, V.A. Kabanov, and Yu.Yu. Marchenko, *Vysokomolek. Soed.*, 1, 94 (1959).
36. B.A. Dolgoplosk, K.L. Makovetsky, E.I. Tinyakova, and O.K. Sharaev, *Polymerization of Dienes under the Effect of π-Allyl Complexes*, Nauka, Moscow, 1968 (in Russian).
37. B.A. Dolgoplosk, *Vysokomolek. Soed.*, 16A, 1171 (1974).
38. B.A. Dolgoplosk, *Vestn. Akad. Nauk SSSR*, No. 11, 95-110 (1977).
39. B.A. Dolgoplosk, T.G. Golenko, K.L. Makovetsky, I.A. Oreshnik, and E.I. Tinyakova, *Dokl. Akad. Nauk SSSR*, 216 807 (1974).
40. B.A. Dolgoplosk, K.L. Makovetsky, E.I. Tinyakova, and I.A. Oreshnik, *Dokl. Akad. Nauk SSSR*, 228, 1109 (1976).
41. S.R. Rafikov, Yu. B. Monakov, G.A. Tolstikov, A.M. Ivanova, M.S. Miftakov, Sh.S. Ramaletdinov, and P.M. Vlasova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7, 1615 (1975).
42. S.R. Rafikov, Yu.B. Monakov, Ya.Kh. Bieshev, I.F. Valitova, Yu.I. Murinov, G.A. Tolstikov, and Yu.E. Nikitin, *Dokl. Akad. Nauk SSSR*, 229, 1174 (1976).
43. V.V. Korshak, T.M. Frunze, V.V. Kurashev, R.B. Shleifman, and L.B. Danilevskaya, *Vysokomolek. Soed.*, 8, 519 (1966).
44. V.V.Korshak, T.M. Frunze, V.I. Zaitsev, V.V. Kurashev, and T.M. Babchinitser, *Vysokomolek. Soed.*, 12A, 416 (1970).
45. V.V. Korshak, T.M. Frunze, S.P. Davtyan, V.V. Kurashev, T.V. Volkova, V.A. Kotel'nikov, and R.B. Shleifman, *Vysokomolek. Soed.*, 21A, 1960 (1979).
46. N.S. Enikolopov and S.A. Vol'fson, *Chemistry and Technology of Polyformaldehyde*, Khimiya, Moscow, 1968 (in Russian).
47. V.A. Ponomarenko, *Vysokomolek. Soed.*, 19A, 1670 (1977).

48. S.G. Entelis and K.S. Kazansky, *Kinetics and Mechanism of Polymerization of Epoxides*, in: *Advances in Chemistry and Physics of Polymers*, Khimiya, Moscow, 1970, pp. 324-385 (in Russian).
49. K.A. Andrianov, *Vysokomolek. Soed.*, **20A**, 243 (1973).
50. K.A. Andrianov, I.I. Tverdokhlebova, S.A. Pavlova, T.A. Larina, and I.I. Petrova, *Vysokomolek. Soed.*, **18A**, 1117 (1976).
51. A.G. Kazakevich, A.A. Zharov, P.A. Yampol'sky, and N.S. Enikolopov, *Dokl. Akad. Nauk SSSR*, 215, 1404 (1974).
52. N.S. Enikolopov and S.A. Vol'fson, *Vestn. Akad. Nauk SSSR*, No. 8, 62 (1976).
53. V.V.Korshak, *Vysokomolek. Soed.*, **16A**, 926 (1974).
54. V.A. Pankratov, S.V. Vinogradova, and V.V. Korshak, *Usp. Khimii*, **46**, 530 (1977).
55. A.K. Bonetskaya, V.V. Ivanov, M.A. Kravchenko, V.A. Pankratov, Ts.M. Frenkel', V.V. Korshak, and S.V. Vinogradova, *Vysokomolek. Soed.*, **22A**, 766 (1980).
56. V.V. Korshak, V.A. Sergeev, and Yu.A. Chernomordik, *Vysokomolek. Soed.*, **19B**, 493 (1977).
57. V.V. Korshak, V.A. Sergeev, V.K. Shitikov, M.E. Vol'pin, and I.S. Kolomnikov, *Dokl. Akad. Nauk SSSR*, **201**, 112 (1971).
58. V.A. Sergeev, Yu.A. Chernomordik, E.B. Sokolova, M.P. Shebanova, A.S. Kurapov, and V.V. Korshak, *Vysokomolek. Soed.*, **21B**, 546 (1979).
59. V.V. Korshak and S.V. Vinogradova, *Equilibrium Polycondensation*, Nauka, Moscow, 1968 (in Russian).
60. G.S. Petrov, I.P. Losev, and B.N. Rutovsky, *Technology of Synthetic Matertals and Plastics*, Goskhimizdat, Moscow-Leningrad, 1946 (in Russian).
61. A.Ya. Ardashnikov, I.E. Kardash, and A.N. Pravednikov, *Vysokomolek. Soed.*, **13A**, 1863 (1971).
62. E.V. Pykhtina, N.P. Glukhoedov, I.E. Kardash, and A.N. Pravednikov, *Zh. Fiz. Khimii*, 52, 1217 (1978).
63. I.E. Kardash, A.Ya. Ardashnikov, S.V. Lavrov, and A.N. Pravednikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7, 1660 (1979).
64. I.E. Kardash, A.Ya. Ardashnikov, S.V. Lavrov, and A.N. Pravednikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 9, 2155 (1979).
65. S.V. Lavrov, I.E. Kardash, and A.N. Pravednikov, *Dokl. Akad. Nauk SSSR*, 239, 126 (1978).
66. S.V. Lavrov, I.E. Kardash, and A.N. Pravednikov, in: *Chemical Kinetics and Catalysis*, Nauka, Moscow, 1979, p. 50 (in Russian).
67. S.V. Lavrov, O.B. Talankina, V.D. Volob'yov, A.L. Izyumnikov, I.E. Kardash, and A.N. Pravednikov, *Vysokomolek. Soed.*, **22A**, 1886 (1980).
68. N.A. Koton, *Vysokomolek. Soed.*, **13A**, 1348 (1971).
69. L.N. Korzhavin, N.R. Prokopchuk, Yu.G. Baklagina, F.S. Florinsky, N.V. Efanova, A.M. Dubnova, S.Ya. Frenkel', and M.M. Koton, *Vysokomolek. Soed.*, **18A**, 707 (1976).
70. B.A. Zhubanov, P.E. Messerle, and V.A. Solomin, *Vysokomolek. Soed.*, **17B**, 560 (1975).
71. B.A. Zhubanov, *Vysokomolek. Soed.*, **20A**, 713 (1978).
72. S.V. Vinogradova, Ya.S. Vygodsky, and V.V. Korshak, *Vysokomolek. Soed.*, **12A**, 1987 (1970).
73. S.V. Vinogradova, Ya.S. Vygodsky, V.V. Korshak, and N.A. Churochkina, *Vysokomolek. Soed.*, **19B**, 93 (1977).
74. Ya.S. Vygodsky, T.N. Spirina, P.P. Nechaev, L.I. Chudina, G.E. Zaikov, V.V. Korshak, and S.V. Vinogradova, *Vysokomolek. Soed.*, **19A**, 1516 (1977).
75. V.V. Korshak and S.V. Vinogradova, *Non-equilibrium Polycondensation*, Nauka, Moscow, 1972 (in Russian).
76. V.A. Vasnev and S.V. Vinogradova, *Usp. Khimii*, **48**, 30 (1979).

77. L.B. Sokolov, *The Fundamentals of Synthesis of Polymers by the Polycondensation Method*, Khimiya, Moscow, 1979 (in Russian).
78. L.B. Sokolov, V.D. Gerasimov, V.M. Savinov, and V.K. Belyakov, *Heat-resistant Aromatic Polyamides*, Khimiya, Moscow, 1975 (in Russian).
79. S.I. Kuchanov, *Methods of Kinetic Calculations in the Chemistry of Polymers*, Khimiya, Moscow, 1978 (in Russian).
80. V.A. Vasnev and S.I. Kuchanov, *Usp. Khimii*, 42, 2194 (1973).
81. S.I. Kuchanov, M.L. Keshtov, P.G. Khalatur, V.A. Vasnev, S.V. Vinogradova, and V.V. Korshak, *Dokl. Akad. Nauk SSSR*, 261, 1164 (1981).
82 V.V. Korshak, M.M. Teplyakov, D.M. Kakauridze, D.A. Shapiro, and E.L. Bulakh, *Vysokomolek. Soed.*, 16A, 1831 (1976).
83. V.V. Korshak, M.M. Teplyakov, and D.M. Kakauridze, *Vysokomolek. Soed.*, 21A, 1601 (1979).
84. V.V. Korshak, M.M. Teplyakov, and R.A. Dvorikova, *Vysokomolek. Soed.*, 24A, 277 (1982).
85. P.P. Shorygin, *The Chemistry of Cellulose*, Goskhimizdat, Moscow, 1939 (in Russian).
86. S.N. Ushakov, Polyvinyl Alcohol and its Derivatives, *Izd. Akad. Nauk SSSR*, Leningrad, 1960, vol. 1 (in Russian).
87. N.A. Plate, A.D. Litmanovich, and O.V. Noa, *Macromolecular Reactions*, Khimiya, Moscow, 1977 (in Russian).
88. N.A. Plate and A.D. Litmanovich, *Vysokomolek. Soed.*, 14A, 2503 (1972).
89. V.A. Kabanov, O.V. Kargina, and V.A. Petrovskaya, *Vysokomolek. Soed.*, 13A, 348 (1971).
90. I.M. Papisov, V.A. Kabanov, E.M. Osada, Loskamo Brito, Raimont J., and A.N. Gvozdetsky, *Vysokomolek. Soed.*, 14A, 2462 (1972).
91. I.M. Papisov, Ts.I. Nedyalkova, N.K. Avramchuk, and V.A. Kabanov, *Vysokomolek. Soed.*, 15A, 2003 (1973).
92. I.M. Papisov, V.Yu. Baranovsky, E.I. Sergieva, A.D. Antipina, and V.A. Kabanov, *Vysokomolek. Soed.*, 16A, 1133 (1974).
93. V.A. Kabanov, V.P. Evdakov, and A.D. Antipina, *Molecular Biology*, 11, 582 (1977).
94. V.V. Korshak, A.A. Askadsky, I.I. Vointseva, B.B. Mustafaeva, A.P. Suprun, and G.L. Slonimsky, *Vysokomolek. Soed.*, 23A, 1002 (1981).
95. V.V. Korshak, G.L. Berestnyova, S.A. Astaf'yev, A.Zh. Taova, and E.P. Gurkova, *Dokl. Akad. Nauk SSSR*, 245, 1118 (1979).
96. E.I. Kardash, A.Ya. Ardashnikov, V.S. Yakubovich, G.I. Braz, A.Ya. Yakubovich, and A.N. Pravednikov, *Vysokomolek. Soed.*, 9A, 1914 (1967).
97. I.E. Kardash, A.Ya. Ardashnikov, F.S. Yakushin, and A.N. Pravednikov, *Vysokomolek. Soed.*, 17A, 598 (1975).
98. N.N. Barashkov, L.A. Zimina, E.N. Teleshov, and A.N. Pravednikov, *Dokl. Akad. Nauk SSSR*, 240, 847 (1978).
99. S.G. Tadevosyan, N.N. Voznesenskaya, I.V. Vasil'yeva, E.N. Teleshov, and A.N. Pravednikov, *Vysokomolek. Soed.*, 20A, 937 (1980).
100. N.M. Emanuel', *Usp. Khimii*, 48, 2113 (1979).
101. G.E. Zaikov, *Usp. Khimii*, 44, 1805 (1975).
102. Yu.V. Moiseev, V.S. Markin, and G.E. Zaikov, *Usp. Khimii*, 45, 510 (1976).
103. S.D. Razumovsky and G.E. Zaikov, *Ozone and its Reactions with Organic Compounds*, Nauka, Moscow, 1974 (in Russian).
104. A.A. Popov and G.E. Zaikov, *Dokl. Akad. Nauk SSSR*, 244, 1178 (1979).
105. A.A. Popov, V.M. Parfyenov, G.A. Krashennikova, and G.E. Zaikov, *Dokl. Akad. Nauk SSSR*, 248, 396 (1979).
106. A.A. Popov, B.E. Krisyuk, N.N. Blinov, and G.E. Zaikov, *Dokl. Akad, Nauk SSSR*, 253, 1169 (1980).
107. G.B. Pariisky, E.Ya. Davydov, and D.Ya. Toptygin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 5, 1054 (1973).

108. Yu.A. Mikheev, T.S. Popravko, L.L. Yasina, and D.Ya. Toptygin, *Vysokomolek. Soed.*, 15A, 2470 (1973).
109. O.A. Ledneva, Yu.A. Mikheev, and D.Ya. Toptygin, *Vysokomolek. Soed.*, 17A, 546 (1975).
110. N.M. Emanuel', V.A. Roginsky, and A.D. Buchachenko, *Usp. Khimii*, 51, 361 (1982).
111. V.Ya. Shlyapintokh, *Plast. Massy*, No. 2, 47 (1976).
112. O.N. Karpukhin and E.M. Slobodetskaya, *Usp. Khimii*, 42, 391 (1973).
113. I.A. Serenkova and Yu.A. Shlyapnikov, *Vysokomolek. Soed.*, 24A, 808 (1982).
114. G.P. Gladyshev and V.F. Tsepalov, *Usp. Khimii*, 44, 1830 (1975).
115. V.V. Ershov, A.A. Volod'kin, and G.A. Nikiforov, *Sterically Hindered Phenols*, Khimiya, Moscow, 1972 (in Russian).
116. E.G. Rozantsev, *Free Iminoxy Radicals*, Khimiya, Moscow, 1970 (in Russian).
117. K.S. Minsker, Al.Al. Berlin, D.V. Kazachenko, and R.G. Abdulina, *Dokl. Akad. Nauk SSSR*, 203, 881 (1972).
118. B.B. Troitsky, L.S. Troitskaya, and N.F. Lepaev, *Dokl. Akad. Nauk SSSR*, 210, 877 (1973).
119. V.S. Pudov and R.A. Papko, *Vysokomolek. Soed.*, 16A, 1409 (1974).
120. V.V. Korshak, *Thermostable Polymers*, Nauka, Moscow, 1969 (in Russian).
121. V.V. Korshak, S.A. Pavlova, P.N. Gribkova, I.V. Vlasova, T.V. Lekae, A.L. Rusanov, and E.S. Krongauz, *Vysokomolek. Soed.*, 22B, 916 (1980).
122. V.B. Gavalyan, I.V. Zhuravlyova, S.A. Pavlova, V.I. Nedel'kin, and V.A. Sergeev, *Vysokomolek. Soed.* 22A, 2121 (1980).
123. I.V. Zhuravlyova, V.M. Laktionov, S.A. Pavlova, S.N. Salazkin, and S.R. Rafikov, *Vysokomolek. Soed.*, 21B, 628 (1979).
124. Yu.L. Avetisyan, P.N. Gribkova, S.A. Pavlova, and I.A. Gribova, *Vysokomolek. Soed.*, 21A, 502 (1979).
125. L.I. Danilina, E.N. Teleshov, and A.N. Pravednikov, *Vysokomolek. Soed.*, 16A, 581 (1974).
126. L.I. Danilina, S.A. Motov, and A.N. Pravednikov, *Vysokomolek. Soed.*, 17A, 2597 (1975).
127. V.A. Orlov and O.G. Tarakanov, *Vysokomolek. Soed.*, 8, 1139 (1966).
128. Yu.I. Matveev, A.A. Askadsky, I.V. Zhuravlyova, G.A. Slonimsky, and V.V. Korshak, *Vysokomolek. Soed.*, 23A, 2013 (1981).
129. V.V. Korshak, A.A. Askadsky, G.L. Slonimsky, S.L. Sosin, L.I. Zakharkin, A.I. Kovredov, B.A. Antipova, and Zh.S. Shaugumbekova, *Vysokomolek. Soed.*, 23A, 2051 (1981).
130. A.A. Berlin, *Dokl. Akad. Nauk SSSR*, 110, 401 (1956).
131. V.E. Gul', L.I. Bulatnikova, O.N. Beletskaya, E.V. Ermakova, and L.V. Bykova, *Vysokomolek. Soed.*, 18A, 118 (1976).
132. N.K. Baramboim, *Mechanochemistry of High Molecular Weight Compounds*, Khimiya, Moscow, 1978 (in Russian).
133. S.V. Vinogradova and Ya.S. Vygodsky, *Usp. Khimii*, 42, 1225 (1973).
134. P.M. Valetsky and I.P. Storozhuk, *Usp. Khimii*, 48, 75 (1979).
135. V.V. Korshak, T.M. Frunze, V.V. Kurashev, and L.B. Danilevskaya, *Vysokomolek. Soed.*, 18A, 848 (1976).
136. V.V. Korshak, *Raznozvennost' of Polymers*, Nauka, Moscow, 1977 (in Russian).
137. G.N. Petrov and A.S. Lykin, *Vysokomolek. Soed.*, 20A, 1203 (1978).
138. I.A. Tutorsky, S.V. Novikov, and B.A. Dogadkin, *Usp. Khimii*, 36, 2026 (1967).
139. A.V. Topchiev and B.A. Krentsel, *Polyolefins—New Synthetic Materials*, Izd. Akad. Nauk SSSR, Moscow, 1963 (in Russian).
140. I.N. Nazarov, *Usp. Khimii*, 14, No. 1, 3-41 (1945).

141. M.F. Shostakovsky, *Vinyl Ethers*, Izd. Akad. Nauk SSSR, Moscow, 1952 (in Russian).
142. V.V. Korshak, A.M. Polyakova, and M.S. Shapiro, *Zh. Vses. Khim. Ob-va im. D.I. Mendeleeva*, 14, 51 (1969).
143. V.V. Korshak, A.N. Polyakova, and K.A. Mager, *Plast. Massy*, No. 1, 44 (1970).
144. V.A. Sergeev, V.K. Shitikov, and V.A. Pankratov, *Usp. Khimii*, 48, 148 (1979).
145. M.M. Teplyakov, *Usp. Khimii*, 48, 344 (1979).
146. V.V. Korshak, V.I. Kasatochkin, N.M. Sladkov, Yu.P. Kudryavtsev, and K. Usenbaev, *Dokl. Akad. Nauk SSSR*, 136, 1342 (1961).
147. W.K. Schitikow, B.A. Kisseljew, W.N. Stepanowa, W.W. Trofimenko, W.W. Korschak, and W.A. Sergejew, *Plast. und Kautsch.*, 21, 734 (1974).
148. G.Sh. Papava, V.A. Sergeev, S.V. Vinogradova, S.V. Abkerova, N.A. Maisuradze, V.V. Korshak, P.D. Tsiskarishvili, and V.K. Shitikov, *Vysokomolek. Soed.*, 16B, 844 (1974).
149. S.I. Siling, *Phenolformaldehyde Oligomers*, in: *The Results of Science and Engineering, Chemistry and Technology of High Molecular Weight Compounds*, VINITI, Moscow, Issue 11, p. 119 (1977).
150. S.A. Artemenko, E.V. Prut, E.F. Oleinik, B.A. Rozenberg, and N.S. Enikolopov, *Dokl. Akad. Nauk SSSR*, 245, 1139 (1979).
151. O.B. Salamatina, R.M. Vinnik, S.A. Artemenko, S.N. Rudnev, E.F. Oleinik, and N.S. Enikolopov, *Vysokomolek. Soed.*, 23A, 2360 (1981).
152. A.A. Berlin, *Usp. Khimii*, 23, 967 (1954).
153. M.G. Gonikberg and B.S. El'yanov, *Dokl. Akad. Nauk SSSR*, 118, 92 (1958).
154. V.A. Ponomarenko, S.P. Krukovsky, and A.Yu. Alybina, *Fluorine-containing Heterochain Polymers*, Nauka, Moscow, 1973 (in Russian).
155. V.A. Sergeev, V.K. Shitikov, and V.I. Nedel'kin, *Polyarylenesulphides—a New Class of Heterochain Polymers*, in: *The Results of Science and Engineering. Chemistry and Technology of High Molecular Weight Compounds*, VINITI, Moscow, Issue 11, p. 53, 1977 (in Russian).
156. V.A. Sergeev and V.I. Nedel'kin, *Vysokomolek. Soed.*, 22A, 309 (1980).
157. V.A. Sergeev, B.I. Nedel'kin, O.V. Andrianova, V.A. Tsyryapkin, and V.V. Yunnikov, *Vysokomolek. Soed.*, 23A, 682 (1981).
158. V.V. Korshak and V.V. Golubev, *Izv. Akad. Nauk SSSR*, OKhN, No. 2, 379 (1949).
159. M.F. Sorokin, E.L. Gershanova, E.I. Stratonova, Z.A. Mikhitarova, N.A. Trubnikova, V.G. Kolesov, and M.M. Lerman, *Lakokras. Materialy i ikh Primenente*, No. 6, 8 (1976).
160. A.A. Berlin, T.Ya. Kefeli, and G.V. Korolev, *Polyetheracrylates*, Nauka, Moscow, 1967 (in Russian).
161. G.S. Petrov, *Carbamide Resins and Pressing Compositions*, MKhTI im. Mendeleeva, Moscow, 1940 (in Russian).
162. V.V. Korshak, T.M. Frunze, and N.G. Matveeva, *Usp. Khimii*, 25, 419 (1956).
163. B.F. Malichenko and E.V. Shelud'ko, *Fluorine-containing Polymers with Nitrogen Atoms in the Chain*, in: *The Results of Science and Engineering. Chemistry and Technology of High Molecular Weight Compounds*, VINITI, Moscow, Issue 4, p. 119, 1973 (in Russian).
164. Yu.S. Lipatov and Yu.Yu. Kercha, *Usp. Khimii*, 46, 320 (1977).
165. T.E. Lipatova, *Catalytic Polymerization of Oligomers and Formation of Polymer Networks*, Dumka, Kiev, p. 207, 1974 (in Russian).
166. V.V. Korshak, *Chemical Structure and Temperature Characteristics of Polymers*, Nauka, Moscow, 1970 (in Russian).
167. N.A. Adrova, M.N. Bessonov, L.A. Laius, and R.P. Rudakov, *Polyimides—A New Class of Heat-resistant Polymers*, Nauka, Moscow, 1968 (in Russian).

168. M.M. Koton, *Vysokomolek. Soed.*, **13A**, 1348 (1971).
169. L.N. Korzhavin, N.R. Prokopchuk, Yu.G. Baklagina, F.S. Florinsky, N.V. Efanova, A.M. Dubnova, S.Ya. Frenkel, and M.M. Koton, *Vysokomolek. Soed.*, **18A**, 707 (1976).
170. S.V. Vinogradova, Ya.S. Vygodsky, N.A. Churochkina, and V.V. Korshak, *Vysokomolek. Soed.*, **19B**, 93 (1977).
171. S.G. Alekseeva, S.V. Vinogradova, V.D. Vorob'yov, Ya. S. Vygodsky, V.V. Korshak, I.Ya. Slonim, T.N. Spirina, Ya. G. Urman, and L.I. Chudina, *Vysokomolek. Soed.*, **18B**, 803 (1976).
172. S.G. Alekseeva, S.V. Vinogradova, V.D. Vorob'yov, Ya.S. Vygodsky, V.V. Korshak, I.Ya. Slonim, T.N. Spirina, Ya.G. Urman, and L.I. Chudina, *Vysokomolek. Soed.*, **21A**, 2207 (1979).
173. I.V. Vasil'yeva, E.N. Teleshov, A.N. Pravednikov, and L.D. Deryugina, *Dokl. Akad. Nauk SSSR*, **201**, 850 (1971).
174. A.L. Rusanov, *Usp. Khimii*, **48**, 75 (1979).
175. A.I. Izyneev, M.M. Teplyakov, V.G. Samsonova, and A.D. Maximov, *Usp. Khimii*, **36**, 2090 (1967).
176. V.V. Korshak, G.M. Tseitlin, and V.N. Kulagin, *Plast. Massy*, No. 12, 35, (1970).
177. A.L. Rusanov, S.N. Leont'yeva, and Ts.G. Iremiashvili, *Usp. Khimii*, **46**, 151 (1977).
178. V.V. Korshak, A.L. Rusanov, and D.S. Tugushi, *Usp. Khimii*, **50**, 2250 (1981).
179. V.A. Pankratov, S.V. Vinogradova, and V.V. Korshak, *Usp. Khimii*, **46**, 530 (1977).
180. A.Ya. Chernikhov, M.N. Yakovlev, V.A. Isaeva, N.K. Ostrovskaya, Yu.I. Kotov, E.L. Gefter, and A.I. Malyshev, *Plast. Massy*, No. 4, 39 (1980).
181. A.Ya. Chernikhov, M.N. Yakovlev, A.Kh. Bulai, N.N. Shmagina, M.P. Noskova, and E.S. Botvinnik, *Dokl. Akad. Nauk SSSR*, **243**, 941 (1978).
182. K.A. Andrianov, *Zh. Obshch. Khimii*, **8**, 1255 (1938).
183. K.A. Andrianov, *Polymers with Inorganic Main Chains of Molecules*, Izd. Akad. Nauk SSSR, Moscow, 1962 (in Russian).
184. V.V. Korshak and A.A. Zhdanov, *Usp. Khimii*, **44**, 468 (1975).
185. K.A. Andrianov, *Dokl. Akad. Nauk SSSR*, **191**, 347 (1970).
186. N.S. Nametkin, S.G. Durgar'yan, and V.S. Khotimsky, *Vysokomolek. Soed.*, **7**, 184 (1965).
187. E.D. Pozhidaev, Yu.Kh. Shaulov, and L.V. Kozlova, *Zh. Fiz. Khimii*, **45**, 133 (1971).
188. D.Ya. Zhinkin, G.N. Mal'kova, G.K. Korneeva, E.A. Semenova, Zh.V. Gorislavskaya, N.V. Markova, K.K. Popkov, and N.V. Sobolevsky, *Plast. Massy*, No. 6, 22 (1970).
189. A.A. Zhdanov, K.A. Andrianov, and M.M. Levitsky, *Vysokomolek. Soed.*, **18A**, 2264 (1976).
190. V.V. Korshak, S.V. Vinogradova, P.M. Valetsky, and N.I. Bekasova, *Vestn. Akad. Nauk SSSR*, No. 11, 23 (1974).
191. V.V. Korshak, V.A. Zamyatina, and N.I. Bekasova, *Organoboron Polymers*, Nauka, Moscow, 1975 (in Russian).
192. V.V. Korshak, S.V. Vinogradova, D.R. Tur, N.N. Kazarova, L.I. Komarova, L.M. Gilman, *Acta Polymerica*, **30**, 245 (1979).
193. V.V. Korshak, S.V. Vinogradova, D.R. Tur, and N.N. Kazarova, *Acta Polymerica*, **31**, 568 (1980).
194. V.V. Korshak, A.I. Solomatina, N.I. Bekasova, M.A. Andreeva, E.G. Bulycheva, S.V. Vinogradova, V.N. Kalinin, and L.I. Zakharkin, *Vysokomolek. Soed.*, **22A**, 1988 (1980).
195. K.M. Saldadze, *Ion-exchange Resins*, Izd. Akad. Nauk. SSSR, 1959 (in Russian).
196. V.A. Davankov, S.V. Rogozhin and A.V. Semechkin, *Ligand-exchange*

Chromatography, in: *The Results of Science and Engineering, Chemistry and Technology of High Molecular Weight Compounds*, VINITI, Moscow, Issue 4, 1973, p. 5 (in Russian).
197. S.V. Rogozhin, V.A. Davankov, and I.I. Pesyakas, *The Latest Achievements in Chromatographic Splitting of Racemates*, in: *The Results of Science and Engineering, Chemistry and Technology of High Molecular Weight Compounds*, VINITI, Moscow, Issue 4, 1973, p. 45 (in Russian).
198. V.A. Davankov, S.V. Rogozhin, and M.P. Tsyurupa, *Vysokomolek. Soed.*, **15B**, 463 (1973).
199. V.A. Davankov, A.V. Volynskaya, and M.P. Tsyurupa, *Vysokomolek. Soed.*, **22B**, 746 (1980).
200. T.E. Lipatova and G.A. Pkhakadze, *Polymers in Surgery*, Dumka, Kiev, 1977 (in Russian).
201. *Chemistry and Technology of Medico-biological Polymers. The Results of Science and Engineering, Chemistry and Technology of High Molecular Weight Compounds*, VINITI, Moscow, Issue 16, 1973 (in Russian).
202. V.A. Kabanov, *Zh. Vses. Khim. Ob-va im. D.I. Mendeleeva*, **27**, 417 (1982).
203. S.P. Papkov, and V.G. Kul'chikhin, *Liquid Crystalline State of Polymers*, Khimiya, Moscow, 1977 (in Russian).
204. A.A. Berlin, *Vysokomolek. Soed.*, **15A**, 256 (1973).
205. A.A. Berlin, M.A. Geiderikh, B.E. Davydov, V.A. Kargin, G.P. Karpacheva, B.A. Krentsel, and G.V. Khutoreva, *The Chemistry of Polyconjugated Systems*, Khimiya, Moscow, 1972 (in Russian).
206. Z.A. Rogovin, *The Chemistry of Cellulose*, Khimiya, Moscow, 1972 (in Russian).
207. Z.A. Rogovin, *Chemical Transformations and Modification of Cellulose*, Khimiya, Moscow, 1967 (in Russian).
208. A.D. Virnik, K.P. Khomyakov, and N.F. Skokova, *Usp. Khimii*, **44**, 1280 (1975).

2 Raznozvennost' of High-molecular Compounds

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1. INTRODUCTION

One of the most important problems of modern chemistry is the relationship between the properties of a compound and its chemical structure. This problem acquires particular importance in the field of high molecular compounds since the obtaining of polymers with a desired set of chemical and physical properties is the paramount task of present-day synthetic polymer chemistry. It is quite natural that in order to solve this problem, we must know the conditions that determine the development of the whole set of properties of a polymer [1, 2].

At an early stage in the history of polymer science the notion of polymers as long uniformly constructed macromolecules

$$-(M)_{\infty}$$

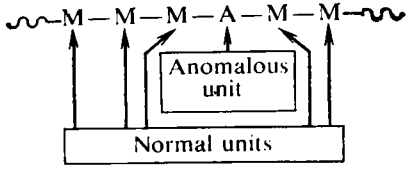
was dominating. However, as information on the structure of polymers accumulated, it became clear that this picture reflects the structure of polymers with insufficient fullness. At present, the necessity of deepening our knowledge on a molecular level and of finding more precise relationships between the properties and structure of polymer macromolecules becomes progressively clear. To achieve these goals, the specific features of the polymer synthesis reactions giving rise to the desired polymer structures are to be known. This is the realm of synthetic chemistry of polymers, one of its main tasks being the control of polymer synthesis reactions aimed at obtaining high molecular compounds whose structure determines the necessary set of physical and chemical properties.

2. THE DEFINITION OF RAZNOZVENNOST' (DIFFERENT-UNIT STRUCTURE) OF POLYMERS

The raznozvennost' (different-unit structure) of polymers is an essential factor of their structure arising from the presence of different anomalous units appearing during synthesis.

We have shown that the presence of anomalous units is a general rule for all polymers known at the present time [1-4].

This is due to the fact that the synthesis of polymers involves a series of consecutive transformations taking place in polymerization, polycondensation, and polymer modification processes accompanied by various secondary transformations. Different changes occurring during the process of synthesis constitute the set of synthetic reactions (leading to the formation of macromolecules) and a variety of side reactions. As a result, anomalous units appear and, in consequence, raznozvenny polymers arise. Consider a number of examples of the formation of anomalous units bringing about raznozvennost' of polymers



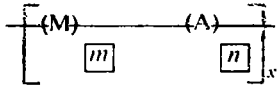
It should be noted first of all that any chemical reaction of low molecular substances is accompanied by the formation of some amount of side products which are removed on purification and therefore do not affect the quality of the main product, the only negative effect consisting in the lowering of the yield. On the contrary, during the formation of polymers all side products remain in the polymer in the form of anomalous units, this process being one of the reasons giving rise to raznozvenny polymers [1-5].

Because of this and also owing to a number of other reasons which will be discussed later, all the methods of synthesis of polymers known at present involve the emergence of raznozvennost' in the polymer structures formed [1-5]. This naturally gives rise to the problem of studying the reaction conditions that allow controlling the degree of raznozvennost', i.e. the quantity and nature of anomalous units in the polymer. At the same time, in some instances it is desirable to synthesize polymers without anomalous units, i.e. chemically homogeneous polymers.

Studies of the properties of raznozvenny polymers led to the conclusion that anomalous units play an essential part in determining the whole set of chemical and physical properties that are peculiar to a given raznozvenny polymer [2]. This suggests the necessity of knowing the effect of the type of anomalous units, their quantity, and their location in the macromolecule on the properties of the polymer.

There is no exaggeration in saying that at the modern stage of the development of polymer science the synthesis of polymers is the prevailing direction but the investigation and use of raznozvenny polymers (or polymers with molecular heterogeneity) are no less important because the latter approach is the only method of

solving the diverse problems of modern science and technology. Therefore, although in the general form we represent the formula of a polymer as $-(M)_x-$ where M is the monomer residue, this is an idealized formula which has nothing to do with reality. In actual fact, it is more correct to depict the structure of a real raznozvenny polymer as



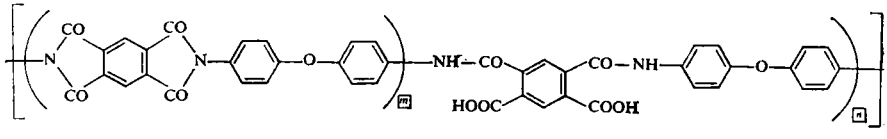
where A are anomalous units and M are normal units [3-5]. Coefficients $\boxed{m}$ and $\boxed{n}$ denote the statistical distribution of the units [5].

Copolymers obtained by copolymerization of two and more unsaturated monomers or formed by polycondensation of a mixture of two and more starting compounds (monomers) and frequently named as mixed polymers belong without exception to raznozvenny polymers by definition [2, 5]. We believe it unsuitable to broaden the concept of copolymers beyond the polymers formed as a result of copolymerization or copolycondensation. For this reason polymer structures emerging as a result of substitution, oxidation, and other reactions are not to be classed with copolymers. It would be more correct to consider these compounds only as raznozvenny polymers since the concept of raznozvenny polymers is broader than that of copolymers. It is expedient to retain the name 'copolymers' for compounds prepared by copolymerization or copolycondensation of two or more monomers because the concept of raznozvenny polymers includes, as one of their types, not only copolymers obtained by normal copolymerization of two or more monomers but also all those polymers where heterogeneous units appeared as a result of side reactions during polymerization and polycondensation processes as well as on substitution in the polymer macromolecule. The composition of raznozvenny polymers is often considered in terms of the microstructure of chain molecules. In this case not only the differences in the composition and structure of the units are taken into account but also the presence of branching, cross-links, the type of chemical bonds between the units, the stereochemical order of the structure of the unit and the macromolecule as a whole, and other features of the structure responsible for the presence of different anomalous units. The specific

features of the structure of this sort have been attracting much attention long since.

This approach has successfully been applied to thermally stable polymers in explaining the dependence of the thermal stability of a large group of polyheteroarylenes on the conditions of their formation and the characteristics of their structure [6].

The discrepancy between the real and the expected thermal stability of some polyheteroarylenes has been exciting the curiosity of researchers for a long time. An analysis of the behaviour of different polymers on heating showed that the main source of the discrepancy lies in the presence of anomalous units leading to the raznozvennost' of polymers [7]. Raznozvenny polyheteroarylenes contain the initial uncyclized units which are anomalous with respect to the basic final structure, as can be seen from the structure of polyimides given as an example:



normal units (cyclized) anomalous units (uncyclized)

These anomalous units are thermally less stable and decompose at lower temperatures than normal, cyclized units; hence, the thermal stability of such raznozvenny polyheteroarylenes containing incompletely cyclized units is lower [6, 7].

Having disclosed a distinct relationship between the structure and the set of chemical and physical properties of polyheteroarylenes, we have also studied this relationship for other classes of polymers and made sure that the disclosed dependences are of a general character [1].

3. COEFFICIENT OF RAZNOZVENNOST'

It appears useful to characterize quantitatively the raznozvennost' of polymers by the coefficient (degree) of raznozvennost' which is defined as the ratio of the amount of anomalous units to that of normal units [1, 2]:

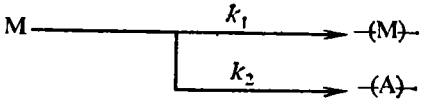
$$K_r = \frac{[A]}{[M]}$$

In a more general case of the synthesis of raznozvenny polymers with anomalous units of different types, this expression will have

the following form:

$$K_r = \frac{[A_1]+[A_2]+[A_3]}{[M]}$$

At the same time, the difference in the rates of the main polymerization or polycondensation reaction and of the side reactions giving rise to anomalous units should be taken into account because this factor determines the concentration of anomalous units in the polymer



In this case, coefficient $K = \frac{K_2}{K_1}$ (where K_1 and K_2 are the rate constants of the reactions) will characterize the ratio of the rates of these two reactions and therefore the amount of anomalous units in the macromolecule of the raznozvenny polymer [1, 2].

4. THE CAUSES OF RAZNOZVENNOST' OF POLYMERS

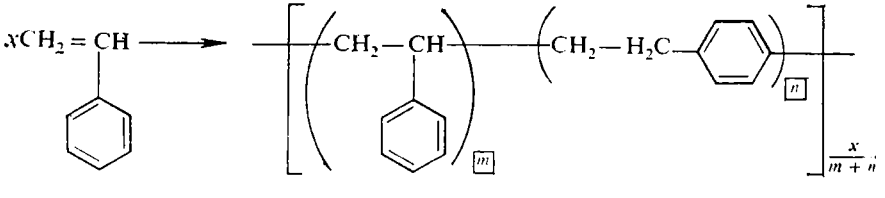
We shall briefly point out the pathways of the formation of different anomalous units giving rise to a variety of raznozvenny polymers.

1. Formation of cross-links, side groups, and various types of branching in the course of polymerization and polycondensation processes.

2. Diverse combinations of the units (particularly of "head-to-head" type) during polymerization and polycondensation.

3. Formation of double bonds in the chain or in the side branches in radical polymerization processes.

4. Incomplete isomerization polymerization of propylene and other olefins (formation of partially isomerized polyolefins)



5. Incomplete isomerization polymerization of styrene (formation of a copolymer of styrene with *p*-xylylene).

6. Emergence of short and long branches caused by chain transfer during polymerization (formation of branched polymers containing tertiary hydrogen or halogen atoms).

7. Monomer isomerization during polymerization and polycondensation (formation of anomalous units of isomeric structure).

8. The difference in the configuration of the asymmetrical carbon atoms making up the units of the macromolecule.

9. The differences in the configuration of the groups with central, axial, and planar asymmetry.

10. The difference in the geometric isomerism of units on diene polymerization (*cis* and *trans* isomerism).

11. The rearrangement of *cis*-isomeric units into *trans*-isomeric ones or vice versa in unsaturated monomers and polymers and also in polymer compounds containing disubstituted cycles.

12. Incomplete trimerization in the polycyclotrimerization reaction of diines and dinitriles.

13. Conformation asymmetry and hindered rotation of units.

14. An unfinished process of the formation of a carbo- or heterocycle in the polycyclization or polycyclocondensation reaction.

15. Copolymerization and copolycondensation processes.

16. Incomplete and irregular substitution and other chemical transformations in the macromolecule during chemical modification of polymers (chlorination, oxidation, dehydration, etc.).

17. Chaotic distribution of cross-links in three-dimensional irregularly cross-linked polymers.

18. Statistical distribution of units with different configuration in atactic polymers.

19. Formation of graft and block copolymers.

20. The presence of aromatic groups in the aliphatic chain and also of aliphatic units among aromatic ones in an irregular arrangement.

21. The presence of hydroaromatic units among aromatic ones as a result of incomplete aromatization or hydrogenation.

22. Different location of substituents in the aromatic, hydroaromatic or heterocyclic ring (*o*-, *m*-, *p*-, etc.).

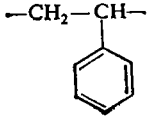
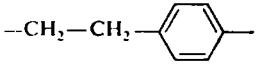
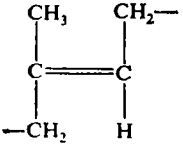
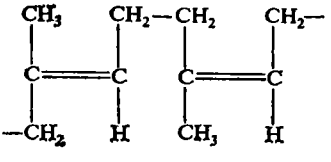
23. Biological processes of the formation and vital activity of cells in the case when the formation of anomalous units in the macromolecules of natural polymers is programmed in the structure of nucleic acids.

24. Disturbances in the natural programmed polycondensation processes (random mutations) giving rise to unprogrammed anomalous units in natural polymers.

25. Random distribution of various isotopes of polymer-forming elements in the macromolecule.

Since raznozvennost' is in principle always caused by the presence of anomalous units, it should be noted that different groups exemplified by Table 1 can serve as these units.

Table 1. Anomalous Groups

Basic formula of the group	Unit formula	Reaction giving rise to the anomalous group
R=	$-CH_2=\underset{\displaystyle R}{\underset{\vert}{CH}}-$	Intramolecular chain transfer
R—	$-CH_2-\underset{\displaystyle (CH_2)_xCH_3}{\underset{\vert}{CH}}-$	Intermolecular chain transfer
—CH=CH—	$-CH_2-CH=CH-CH_2-$	Hydrogen or halogen detachment
—CH=CH_2	$-CH_2-\underset{\displaystyle CH=CH_2}{\underset{\vert}{CH}}-$	Polymerization of dienes in 1,2-position
—CH—	$-CH_2-CH-CH_2-CH_2-$	Polymer cross-linking by ionizing radiation or by chemical means
—CH—	$-CH_2-CH-CH_2-CH_2-$	
—O—O—	$-CH_2-O-O-CH_2-$	Copolymerization with oxygen
—A—	—M—A—M—M—M—	Copolymerization
—CHX—CHX—	$-CH_2-CHX-CHX-CH_2-$	"Head-to-head" arrangement of units
		Monomer isomerization
—M—	—A—M—A—M—M—	Atactic polymerization
		Isoprene polymerization
Cisoid and transoid conformation		Conformational specific polycondensation

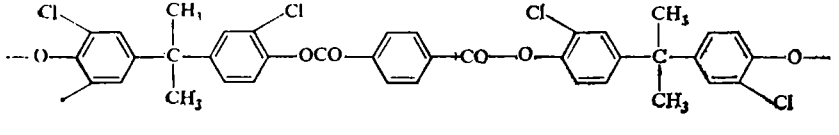
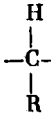
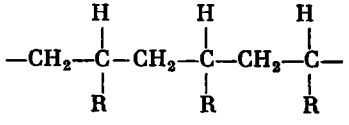
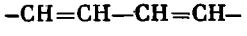
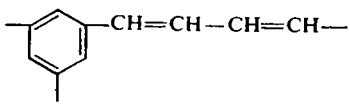
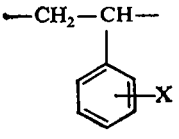
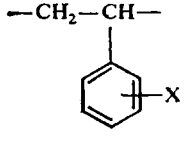
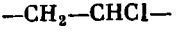
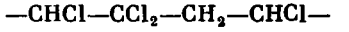
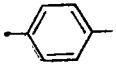
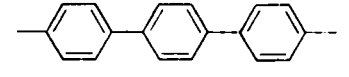
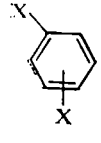
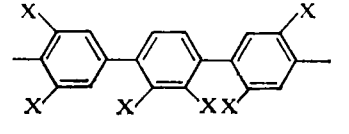


Table 1 (cont.)

Basic formula of the group	Unit formula	Reaction giving rise to the anomalous group
		Stereoregular polymerization
		Polycyclotrimerization of diines
		Incomplete substitution in the phenyl group
		Incomplete substitution on chlorination
		Incomplete aromatization of carbocyclic units
		Different location of substituents as a result of substitution reaction

However, only the group which is randomly distributed in the macromolecule is anomalous. Therefore, for instance, the propanediyl group $-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$ in polypropylene will be a normal unit whereas in polyethylene it will be an anomalous unit (group).

The number of concrete factors leading to raznozvennost' of polymers is rather large. Each of them is quite essential and if we remember that not infrequently several factors act, this may result in their summation and in a high degree of raznozvennost' and hence in a strong effect of the latter on the whole set of physical and chemical properties of polymers [1]. In this context a prob-

lem of the control of the raznozvennost' of polymers arises. Its solution calls for knowing all reactions leading to the formation of anomalous units and to raznozvennost' of polymers [1, 2, 8]. For this reason we shall briefly dwell upon the factors that cause these reactions and on the problem of the control of such reactions.

Needless to say that we shall consider only the reactions that are typical of a certain group of transformations because the analysis of all reactions giving rise to raznozvennost' of polymers is beyond the scope of this paper. A more detailed description of these reactions should be sought for in the already published special reviews and monographs [1, 2, 3, 5, 9, 10].

Table 2. The Set of Polymerization Reactions

The set of polymerization reactions		
	Normal polymerization reactions	Chain initiation
		Chain growth
		Chain termination
	Side reactions giving rise to raznozvenny polymers	Branching of macromolecules
		Partial isomerization of units
		Copolymerization
		Different combinations of units
		Stereospecific polymerization
		Recombination of macroradicals
		Disproportionation of macroradicals
		Partial dehydrogenation of polymers
		Partial dehydrochlorination of polymers
		Partial dehydration of polymers
		Irregular cross-linking of macromolecules
		Steric disorder of units
		Random distribution of the atoms of stable isotopes in the macromolecules of polymers
		Other side reactions

Radical polymerization involves a series of consecutive reactions leading to the formation of a polymer. We shall denote it as a "set of normal polymerization reactions". Chain initiation, growth and termination reactions occurring consecutively during polymerization belong to this set.

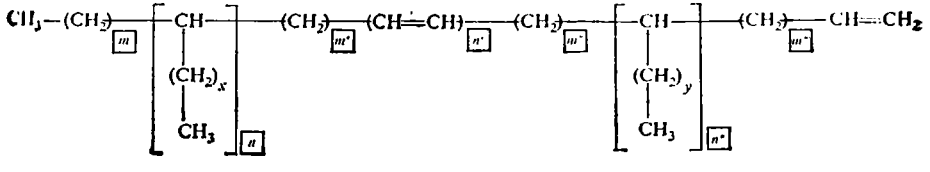
Together with the set of normal polymerization reactions, there exists a "set of side polymerization reactions" bringing about the formation of anomalous units (Table 2).

Characteristic of radical polymerization are such reactions of the formation of anomalous units as branching, recombination, unit isomerization, different combinations of units, steric irregularity, copolymerization, and also reactions resulting in double bonds (dehydrogenation, dehydrochlorination, dehydration, etc.) [11]. All these polymerization side reactions take place simultaneously with the chain growth reaction and are greatly accelerated by temperature rise and by the presence of various salts and other compounds acting as catalysts. These reactions afford polyethylene

whose structure is by no means reflected by the $-(CH_2-CH_2)_x-$

formula, as could be expected on normal polymerization according to the "set of normal polymerization reactions".

Because of the "set of side polymerization reactions", the formula of raznozvenny polyethylene becomes more complex



This formula depicts the direction and the result of side reactions leading to the formation of a series of anomalous units and of a raznozvenny polymer [9, 11].

In ionic and ionic-coordinate polymerization, together with the above-mentioned factors belonging to the set of side polymerization reactions, an important part is played by steric disorder so essential in the case of stereospecific polymerization [11]. Of much significance is catalyst-induced isomerization of units frequently encountered in isomerization polymerization [11].

In polycondensation, the picture undergoes noticeable changes since the character of reactions involved in this case is slightly different, as indicated by Table 3.

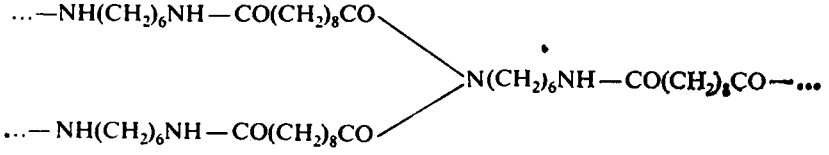
Table 3. The Set of Polycondensation Reactions

The set of polycondensation reactions	Normal polycondensation reactions	Chain initiation
		Chain growth
		Chain termination
	Side polycondensation reactions giving rise to raznozvenny polymers	Branching of macromolecules
		Isomerization of units
		Copolycondensation
		Incomplete cyclization in heteroarylenes
		Irregular cross-linking of macromolecules
		Different combinations of unsymmetrical units
		Stereospecific polycondensation
		Steric disorder of units
		Random distribution of the atoms of stable isotopes in the macromolecules of polymers
		Other side reactions

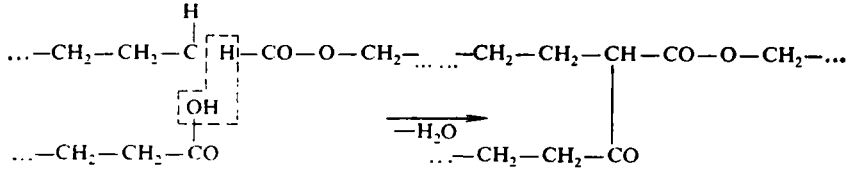
In polycondensation reactions one deals not only with the "set of normal polycondensation reactions" but also with such reactions as the branching of macromolecules, copolycondensation, different combinations of unsymmetrical units, incomplete cyclization of carbo- and heterocycles, stereospecific polycondensation, steric disorder of units, isomerization of units, cross-linking, and other reactions making up the "set of side polycondensation reactions" [12-14].

It should also be borne in mind in this case that the equilibrium [10] and non-equilibrium [15] polycondensation reactions are dissimilar in some transformations. The newly disclosed conformation-specific polycondensation process which affords conformers of polyarylates as individual isomeric compounds different in their properties is worth mentioning [13]. These are examples of raznoz-

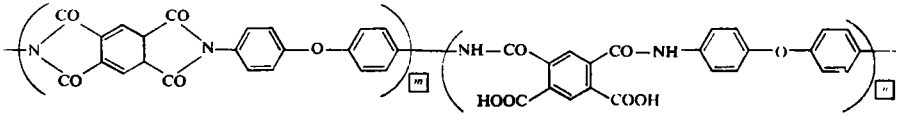
venny polymers obtained by polycondensation



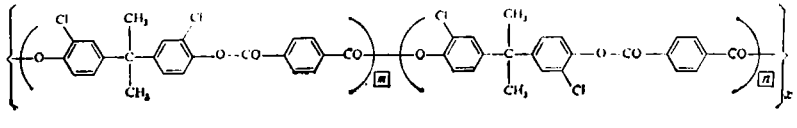
branched polyamide



formation of a branched polyester



raznozvenny polyimide



raznozvenny polyarylate

Table 3 lists the reactions comprising the set of normal and side polycondensation processes. All these reactions are sensitive to temperature and to the concentrations of reactants and are accelerated by salts, solvents, and other catalytically acting substances [14].

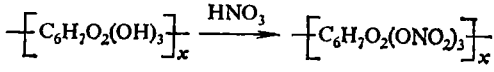
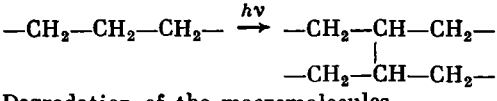
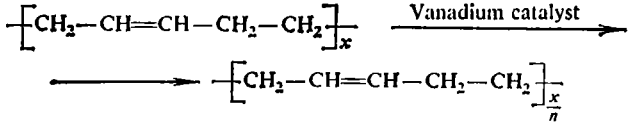
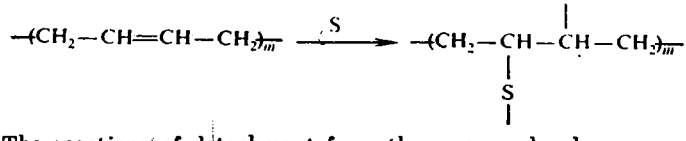
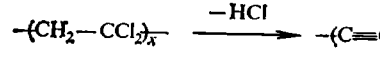
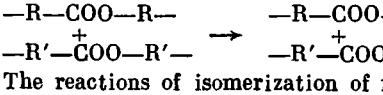
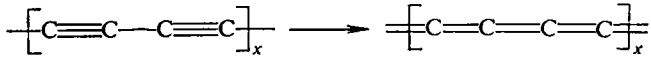
An interesting example of raznozvennost' of polymers resulting from polycondensation is provided by the formation of isomeric conformation-regular polyarylates dissimilar in their properties because of conformational isomerism [13].

It should be noted here that anomalous units are formed in different ways in the processes of equilibrium and non-equilibrium polycondensation [10, 15].

Finally, the third type of synthetic reactions is polymer modification. Table 4 gives typical polymer modification reactions.

It follows from Table 4 that the modification reactions strongly differ from the polymerization and polycondensation reactions,

Table 4. Typical Reactions of Polymer Chemical Modification [16]

No.	Name and equation of the modification reaction
1	Substitution of atoms and groups in the macromolecule 
2	Polymer cross-linking 
3	Degradation of the macromolecules 
4	The reactions of addition to double bonds in the macromolecule 
5	The reactions of detachment from the macromolecules 
6	Exchange reactions of heterochain polymers 
7	The reactions of isomerization of macromolecules 

the difference being determined first of all by the fact that in the modification reactions polymers are the initial substances while in the latter two reactions these are monomers. This feature determines the specific character of each of the reaction groups [16].

Raznozvennost' of polymers in the modification reactions of natural and synthetic polymers can be caused by side reactions, such

Table 5. The Set of Modification Reactions

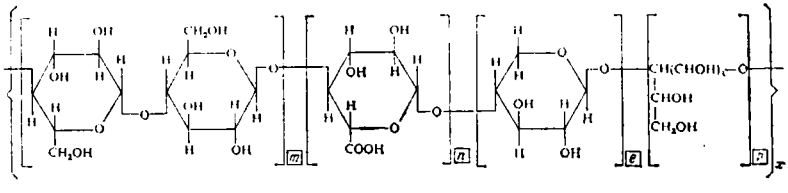
The set of modification reactions	Normal modification reactions	Hydroxyl group replacement
		Hydrogen atom replacement
		Halogen atom replacement
		Polymer cross-linking
		Regular addition to double bonds in the macromolecule
		Exchange reactions of heterochain polymers
		Degradation of the macromolecules
		Detachment of water, hydrogen halide, etc.
		Isomerization of the macromolecules
	Side reactions and other factors giving rise to raznozvenny polymers	Incomplete replacement of the hydroxyl, hydrogen, halogen, etc. in the polymer macromolecule
		Grafting to the macromolecules
		Partial oxidation of the macromolecules
		Irregular cross-linking of the macromolecules
		Partial degradation of the macromolecules
		Incomplete exchange in heterochain polymers
		Statistical distribution of the atoms of stable isotopes in the polymer macromolecules
		Partial cross-linking of the polymer
		Partial addition to double bonds
		Partial detachment of water, hydrogen halide, etc.
		Incomplete isomerization of the macromolecules
		Other side reactions

as incomplete substitution in the macromolecules, the reaction of grafting to the macromolecules, partial oxidation, chlorination and similar reactions of the macromolecules, irregular cross-linking, incomplete exchange in heterochain polymers, and other reactions of different chemical nature [16, 17]. Various modification reactions are listed in Table 5.

It is to be noted that polymer synthesis in nature also involves the formation of raznozvenny polymers, as is the case with the synthesis of rubber, cellulose, polypeptides, nucleic acids, and some other natural polymers.

In natural homopolymers such as cellulose and rubber, whose synthesis takes place in the living cell under control of complex enzymic systems, anomalous units are also present in small quantities; therefore, these polymers can be considered as raznozvennost' of polymers. Cellulose contains open units and natural rubber *trans* units [19].

Thus, the actual formula of cellulose is composed of different units



Polypeptides, polynucleotides, etc. are copolymers and for this reason can be treated as raznozvenny polymers. Besides, anomalous units of random nature are not infrequently present in these polymers; in the case of polynucleotides, such units can be responsible for hereditary diseases.

It can thus be concluded that there is some uncertainty in the synthesis of natural polymers with the result that anomalous units appear and the homopolymers synthesized in nature are not 100% raznozvenny [19].

Among the sources of raznozvennost' of polymers, of great importance is, in our opinion, the statistical distribution of the atoms of isotopes. The elements making up polymer macromolecules are known to have a number of isotopes, as is shown in Table 6.

For this reason, among the whole range of factors giving rise to raznozvennost' of polymers, of much importance is also the presence of randomly distributed atoms of the isotopes of the polymer-forming elements listed above [11].

The effect of isotopes has been shown very vividly using an example of ethylene, propylene, and styrene copolymers with ethylene, propylene, and styrene deuterated to different degrees. Ethylene

Table 6. The Stable Isotopes of the Polymer-forming Elements [11]

Element	The known stable isotopes	Relative distribution, %
Hydrogen	H, D	H—99.98, D—0.016
Boron	^{10}B, ^{11}B	^{10}B—18.8, ^{11}B—81.2
Carbon	^{12}C, ^{13}C	^{12}C—98.9, ^{13}C—1.1
Nitrogen	^{14}N, ^{15}N	^{14}N—99.6, ^{15}N—0.4
Oxygen	^{16}O, ^{17}O, ^{18}O	^{16}O—99.76, ^{17}O—0.4, ^{18}O—0.2
Silicon	^{28}Si, ^{29}Si, ^{30}Si	^{28}Si—92,6, ^{29}Si—4.7, ^{30}Si—3.1
Chlorine	^{35}Cl, ^{37}Cl	^{35}Cl—75.4, ^{37}Cl—24.6

copolymerization with deuteroethylene complied with the following equation [20-24]:

$$m CH_2{=}CH_2 + n CD_2{=}CD_2 \longrightarrow -(CH_2-CH_2)_m-(CD_2-CD_2)_n-$$

The copolymers of propylene and deuteropropylene were obtained by the reaction [22]:

$$m CH_2{=}CH(CH_3) + CD_2{=}CD(CD_3) \longrightarrow \left[\left(CH_2-CH(CH_3)\right)_m\left(CD_2-CD(CD_3)\right)_n\right]_x$$

The synthesis of the copolymers of styrene and deuterated styrenes follows the scheme [23, 24]:

$$m CH_2{=}CH(C_6H_5) + n CD_2{=}CD(C_6D_5) \longrightarrow \left[\left(CH_2-CH(C_6H_5)\right)_m\left(CD_2-CD(C_6D_5)\right)_n\right]_x$$

The effect of the concentration of the hydrogen isotope on the properties of polymers was clearly observed in all copolymers containing different amounts of deuterium. This fact attested to a great importance of isotopes as one of the factors leading to raznozvennost' of polymers.

For instance, it was shown that the substitution of deuterium for hydrogen in polyethylene noticeably changes the set of the physical and chemical properties of the polymer. Such characteristics as density, glass transition temperature, melting temperature, flow temperature, crystallinity, thermal stability, oxidation stability,

etc. are affected [22-24]. Thus, a thorough analysis of the literature and studies of a number of synthetic reactions convinced us in the fact that virtually all methods for obtaining polymers known at present lead to raznozvennost' of polymers [1-6].

The presence of anomalous units should greatly influence the whole set of chemical and physical properties peculiar to the polymer [1, 6]. Here of much importance will be first of all the nature, the number of anomalous units, and the order of their arrangement in the macromolecule.

At the present time the information on the presence and type of raznozvennost' of polymers and on its effect on the chemical and physical properties of the polymer is still extremely insufficient. However, it is known that in some cases an analysis of the synthesis process disclosed the principles which make it possible to control the character and degree of raznozvennost' of the polymers obtained. The following reaction conditions belong to the controlling factors, the temperature of the process, the nature of the solvent, the concentration of the solution, impurities, catalysts, etc. [1]. Thus, there have been found conditions under which polyamides with linear macromolecules or with different branching degrees can be obtained from chlorides of carboranedicarboxylic acids and tetraamines [25].

The influence of the raznozvennost' of polyheteroarylenes on their thermal stability has already been discussed [2, 26]. The effect of the isotopic composition of polymers on their properties has been shown for copolymers of ethylene with deuteroethylene. The physical properties of these copolymers are dependent on the concentration of deuterium to a substantial extent [21-24]. It should also be noted that polyethylene as such is a brilliant example of the great effect of raznozvennost' of polymers on the properties of the polymer. The substantial difference in properties existing between low-density polyethylene, high-density polyethylene, and particularly polymethylene is definitely due to this effect and clearly shows raznozvennost' of polymers to be the substantial factor of polymer structure [16].

On the other hand, it should be emphasized that this example shows that raznozvennost' is a factor whose usefulness in any specific case depends on the nature of the polymer and on the desired results and can play both a positive and a negative part in determining the set of the properties of the synthesized polymer. However, the conclusion that purposefully controlled raznozvennost' of polymers will in a number of cases afford polymers with the desired structure and the required set of physical and chemical properties is unquestionable even now. At the moment our knowledge of the real properties of homochain single-unit polymers is far from full since nobody has succeeded in obtaining them in pure form.

Therefore, the major task of the future is to elucidate the effect of such parameters as the quantity, nature, and distribution of anomalous units and also the influence of different factors leading to raznozvennost' of polymers. Only having clarified these fine particulars of structure and chemical aspects of their origination, we shall have a true idea of the dependence of the properties of polymers on their structure.

We have considered such methods of synthesis of polymers as polymerization, polycondensation, and modification and understood that they all are accompanied by reactions giving rise to anomalous units and hence to raznozvennost' of polymers. From this a conclusion can be drawn that the methods of synthesis of polymers we know of are still highly inadequate.

5. THE EFFECT OF RAZNOZVENNOST' ON THE PROPERTIES OF POLYMERS

One of the most important problems in modern chemistry is undoubtedly the relationship between the properties of a compound and its chemical structure. The significance of this problem manifests itself with particular clearness in the field of high-molecular compounds where the synthesis of substances with a required set of chemical and physical properties is a fundamental task. The solution to the problem inevitably necessitates the knowledge of the dependences which determine the whole set of properties of a given polymer. However, at present we have no information on the properties of homopolymers because all polymer synthesis reactions familiar to us lead to the formation of raznozvenny polymers containing anomalous units. It is the properties of these polymers that are known; their description is dealt with below.

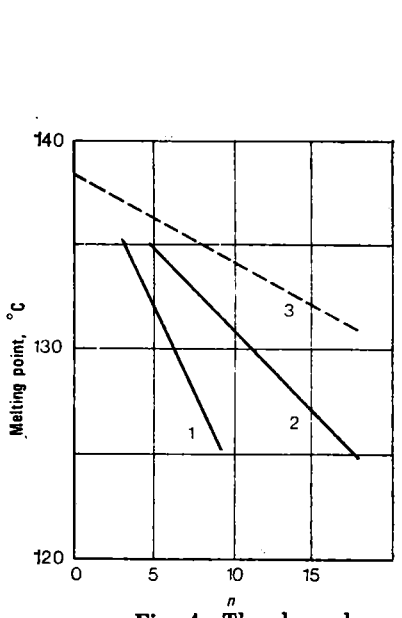
Consider the significance of raznozvennost' of polymers from the viewpoint of the effect of this phenomenon on the whole set of physical and chemical properties of a polymer. The presence of anomalous groups markedly affects the physical properties of a polymer in such a way as to hamper the ordering of the macromolecules; as a result, polymer crystallization becomes difficult, density decreases, glass transition, melting, softening, and flow temperatures go down. Simultaneously with that, solubility and elasticity grow and mechanical strength falls [1, 2, 6, 28].

Figure 1 shows the influence of the degree of raznozvennost' of polyethylene on its melting point [27]. An increase in the number of side groups lowers the melting point; ethyl groups reduce the melting point more intensely than methyl groups.

The melting point of copolymers is most commonly lower than that of homopolymers although exceptions also exist. Figure 2 presents the dependence of the melting point of polyamides on their

raznozvennost', which confirms this rule [31]. The same dependence is also observed for a number of copolymers prepared from vinyl monomers, as is seen from Fig. 3 giving glass transition temperatures of some copolymers [32].

The chemical properties of raznozvenny polymers also differ from those of similar-unit homopolymers. This difference is first



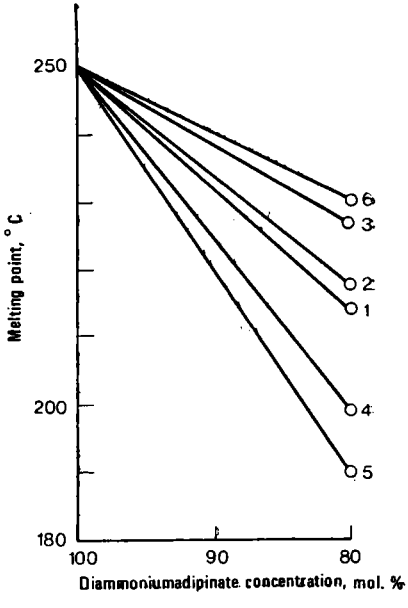


Fig. 1. The dependence of the melting point of branched polymethylenes on the number of side groups:
1—ethyl groups, *2*—methyl groups, *3*—theoretical curve (Flory's formula), *n*—the number of branchings per 1000 carbon atoms

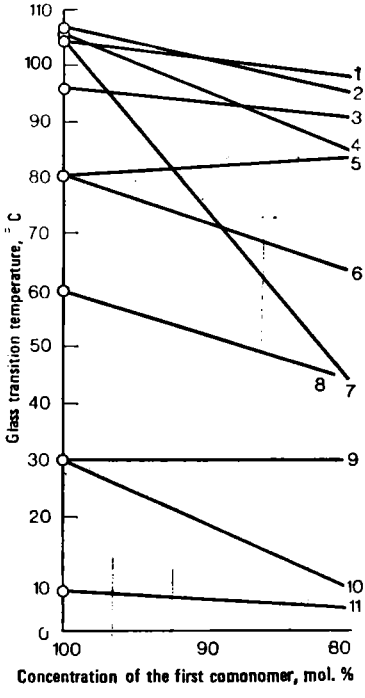
Fig. 2. The dependence of the melting point of mixed polyamides on the nature and amount of the second component. The mixed polyamides were obtained from hexamethylenediammonium adipate and a corresponding comonomer. Comonomer:
1—hexamethylenediammonium azelate, *2*—hexamethylenediammonium sebacate, *3*—hexamethylenediammonium pimelate, *4*—*m*-phenylenediammonium adipate, *5*—*m*-toluylenediammonium adipate, *6*—ω-aminoenanthic acid

of all expressed in a higher reactivity of raznozvenny polymers in relation to chlorination, oxidation, and degradation reactions caused by the presence of tertiary hydrogen atoms at branches and in groups attached in a "head-to-head" order [2, 3].

Stereoregular polymers prove to be thermally more stable than atactic polymers with a similar structure. Exactly the same picture is observed in polyheteroarylenes whose thermal stability is

lowered by the presence of "defective" uncyclized units [2, 3]. The latter begin to decompose at lower temperatures, thus reducing the thermal stability of polyheteroarylenes [29, 30].

Figure 4 illustrates the dependence of the thermal stability of polymers on their degree of branching [33]. Branched polymers



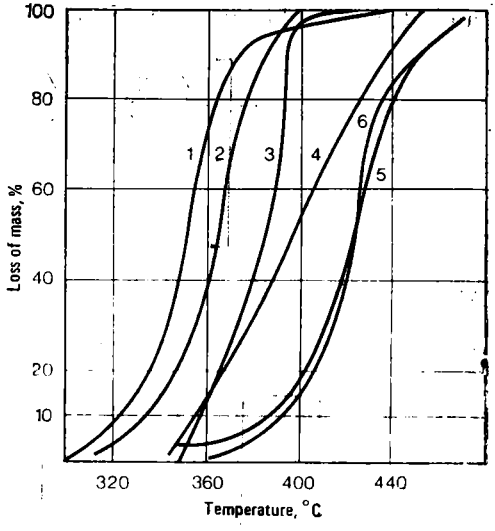


Fig. 3. The dependence of the glass transition temperature of copolymers on the nature and amount of the second comonomer. Copolymer:

1—methyl methacrylate with styrene, *2*—acrylonitrile with methyl methacrylate, *3*—styrene with methyl methacrylate, *4*—methyl methacrylate with acrylonitrile, *5*—vinyl chloride with acrylonitrile, *6*—vinyl chloride with vinyl acetate, *7*—methyl methacrylate with butyl acrylate, *8*—ethyl methacrylate with butyl acrylate, *9*—butyl acrylate with ethyl methacrylate, *10*—butyl methacrylate with methyl acrylate, *11*—methyl acrylate with butyl methacrylate

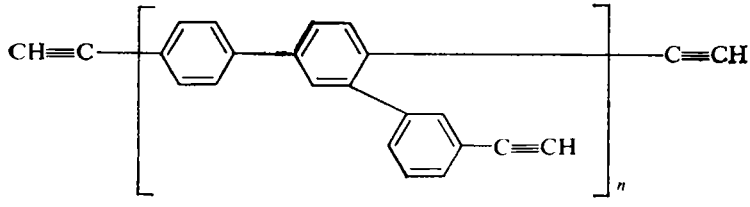
Fig. 4. Thermal decomposition of polymers:

1—polyisoprene, *2*—polyisobutylene, *3*—polystyrene, *4*—copolymer of styrene with butadiene, *5*—polybutadiene, *6*—polyethylene

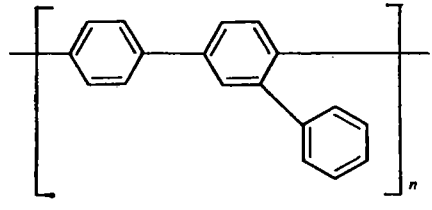
decompose at lower temperatures than linear polymers, evidently because of the splitting of the side groups present in them in large quantities.

Here is another example of the influence of side groups on the thermal stability of polymers. Polyphenylene obtained in an acet-

ylene polycyclotrimerization reaction has the following structure [34]:



The ethynyl groups reduce its thermal stability. After oxidation and decarboxylation, the following polyphenylene emerges:



which is thermally much more stable (Fig. 5).

Studies of the degradation kinetics of methyl methacrylate copolymers with citraconic amide, methyl acrylamide, methylol

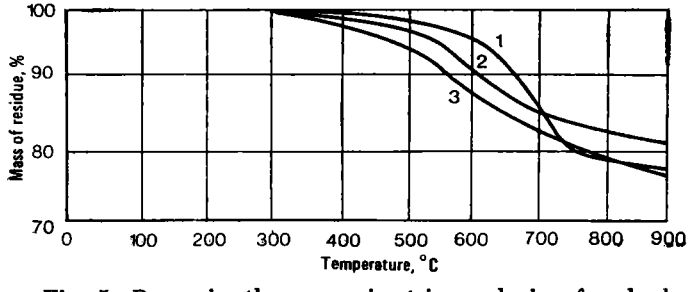


Fig. 5. Dynamic thermogravimetric analysis of polyphenylenes in helium atmosphere:

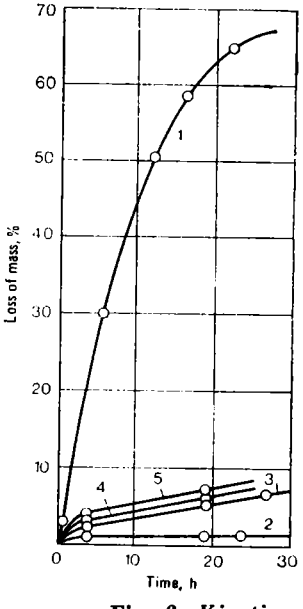
1—polyphenylene with no defective ethynyl groups, *2*—polyphenylene obtained from diethynyl benzene, *3*—polyphenylene obtained from diethynyl benzene and phenyl acetylene

methacrylamide, and methacrylic acid (the results are presented in Fig. 6) show that copolymers decompose much slower than the homopolymer [35].

The traces of dynamic thermogravimetric analysis of polyhydrazides with various cyclization degrees (Fig. 7) indicate the growth of thermal stability of polyoxadiazoles as the cyclization process

goes on [36]. Besides, this process leads to the growth of the activation energy of the reaction (Fig. 8) [36].

An interesting example of the effect of raznozvennost' of polymers on the thermal stability of polymers is provided by pyrrones



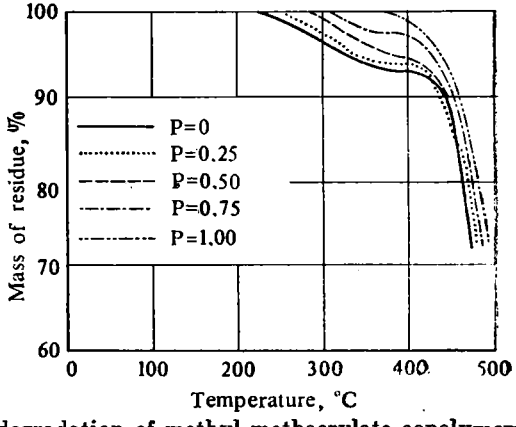


Fig. 6. Kinetics of degradation of methyl methacrylate copolymers in air at 200 °C:

1—polymethylmethacrylate, *2*—copolymer of methyl methacrylate with citraconamide (40%), *3*—same, with methyl methacrylate (40%), *4*—same, with methylol methacrylamide (7%), *5*—same, with methacrylic acid (15%)

Fig. 7. Dynamic thermogravimetric analysis of a polyhydrazide with different cyclization degree (*P*)

[37]. The thermal stability of pyrrones depends on the concentration of uncyclized units whose presence reduces the decomposition temperature of the polymers (Fig. 9).

It can be seen from Fig. 9 that the decomposition of the polyaminoamido acid starts at about 100-150 °C whereas that of pyrrone occurs at 400 °C. Their decomposition is determined by the stability of uncyclized units. It can be seen from Fig. 10 showing the liberation of water and carbon dioxide on the heating of the polyaminoamido acid and pyrrone [37] that the decomposition of pyrrone begins at higher temperatures (by 100-200 °C) and is less intense, thus providing a higher thermal stability of pyrrone and illustrating the possibility of its lowering in the presence of uncyclized units of a polyaminoamido acid.

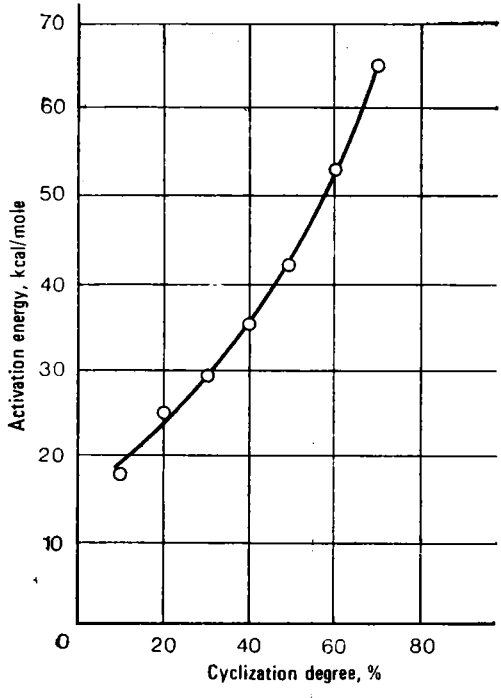


Fig. 8. The variation of activation energy in the course of the dehydrocyclization reaction of polyhydrazides

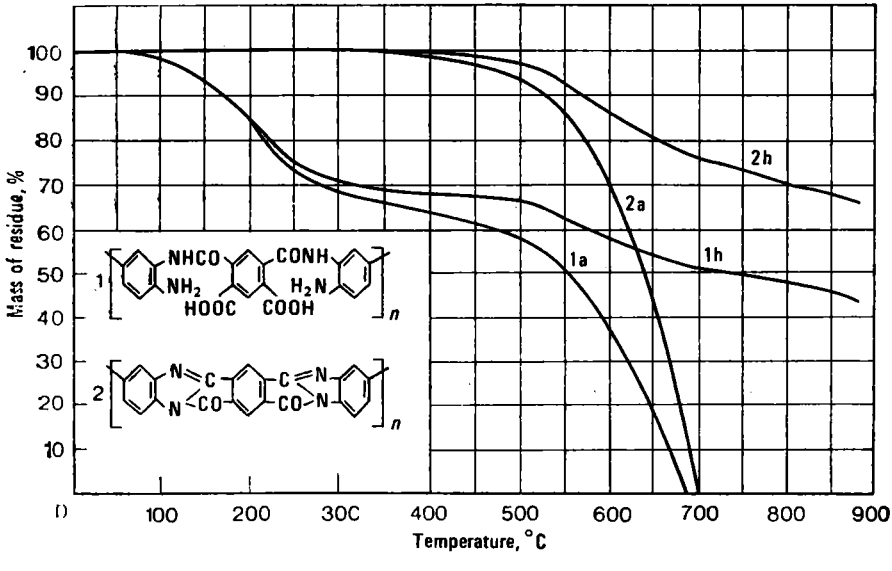
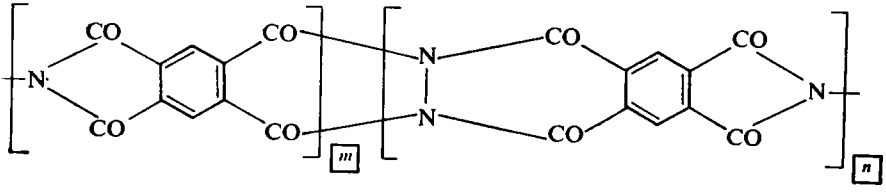


Fig. 9. Dynamic thermogravimetric analysis of a polyaminoamido acid (*1*) and pyrrone (*2*) in air (a) and in helium atmosphere (h)

Yet another example of raznozvenny polymers is exhibited by a polyimide obtained by polycondensation of hydrazine with pyromellitic anhydride; the formula of the polyimide can be presented as follows:



Depending on the reaction conditions, a polymer containing five- or six-membered heterocycles can be obtained [38]. These polymers strongly differ in thermal stability (Fig. 11).

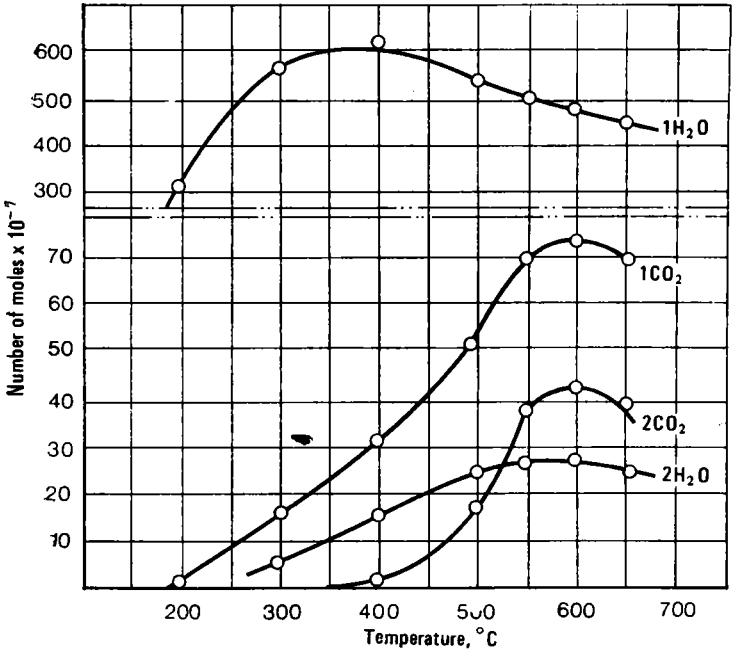


Fig. 10. Liberation of water and carbon dioxide in pyrolysis of a polyaminoamido acid (*1*) and pyrrone (*2*)

Thus, there is every reason to conclude that raznozvennost' of polymers is a factor raising their reactivity and lowering thermal stability.

The dependence of polymer properties on the degree and character of raznozvennost' should be considered with due regard for

service conditions and the character of requirements imposed on them. Therefore, it should be once again emphasized that in some cases raznozvennost' will be a negative factor worsening the param-

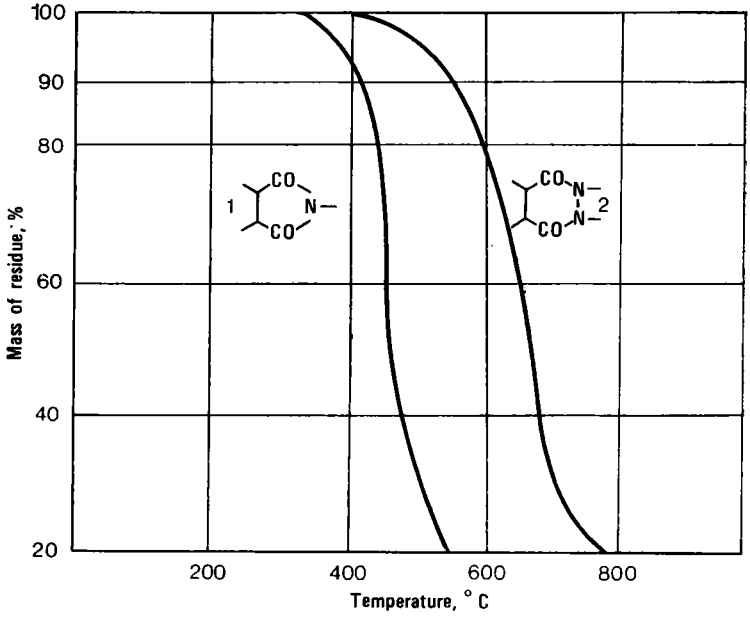


Fig. 11. Dynamic thermogravimetric analysis of polyimides with five-membered (*1*) and six-membered (*2*) rings

eters of the polymer while in others it will be an advantageous feature because it improves the characteristics of a certain polymer [2, 3].

The first case, evidently, pertains to the use of a polymer under extreme conditions, i.e. when it should display the highest characteristics (high thermal stability, oxidation resistance, resistance to solvents, and high mechanical strength). In these cases a low degree of raznozvennost' seems to be desirable since it is a negative factor. Raznozvennost' will be naturally a positive factor when the solubility and elasticity of the polymer are to be improved or its melting and softening points decreased, which also happens rather frequently [2, 3].

Since the phenomenon of raznozvennost' is based on a series of side reactions taking place in the course of polymer synthesis by polymerization and polycondensation methods as well as modification, different polymers can be obtained from the same monomer by purposefully controlling the direction and intensity of these side reactions.

6. CONCLUSION

Ending the discussion of the raznozvennost' problem and related questions in polymer chemistry, we can make a conclusion about immense importance of the problem for a correct understanding of the polymer synthesis processes and of a relationship between their properties and structure.

Thorough analysis of the set of reactions occurring during polymer synthesis by polymerization, polycondensation, and modification methods leads to a conclusion about the existence of a series of side reactions accompanying each of these processes; these reactions give rise to various anomalous units and hence to raznozvenny polymers. As a result, raznozvennost' turns out to be an indispensable attribute of all polymer types known at present so that polymers should be regarded as raznozvenny. All known types of anomalous units and reactions leading to their formation are classified and their great variety is shown.

Raznozvennost' of polymers is shown to affect strongly the whole set of physical and chemical properties of polymers and in this context it should be taken into account as an essential factor.

An analysis of the effect of raznozvennost' of polymers on the properties of polymers made it possible to claim that raznozvennost' of polymers can be both a positive and a negative factor, depending on the nature of the polymer, the type of raznozvennost', and the required set of properties of the polymer.

Special emphasis is made on the fact that side reactions giving rise to anomalous units and raznozvennost' can be used for preparing polymers with the desired set of properties.

References

1. V.V. Korshak, *Raznozvennost' of Polymers*, Moscow, Nauka, 1977 (in Russian).
2. V.V. Korshak, *Vysokomolek. Soed.*, 19A, 1179 (1977).
3. V.V. Korshak, *International Microsymposium on Polycondensation, Abstracts of Papers*, Kiev, 1971.
4. V.V. Korshak, *Vysokomolek. Soed.*, 15A, 298 (1973).
5. V.V. Korshak, *Usp. Khimii*, 42, 695 (1973).
6. V.V. Korshak, *Chemical Structure and Temperature Characteristics of Polymers*, Moscow, Nauka, 1970, pp. 376-379 (in Russian).
7. V.V. Korshak, Yu.E. Doroshenko, and V.A. Khomutov, *Vysokomolek. Soed.*, 15A, 2020 (1973).
8. P.P. Nechaev, Ya.S. Vygodsky, G.E. Zaikov, and S.V. Vinogradova, *Vysokomolek. Soed.*, 18A, 1667 (1976).
9. V. V. Korshak, *Vysokomolek. Soed.*, 18A, 1443 (1976).
10. V.V. Korshak and S.V. Vinogradova, *Equilibrium Polycondensation*, Moscow, Nauka, 1968 (in Russian).
11. V.V. Korshak and N.M. Kozyreva, *Usp. Khimii*, 48, 5 (1979).

12. V.V. Korshak, *Raznozvennost' of Polymers*, Moscow, Nauka, 1977, p. 18 (in Russian).
13. V.V. Koršak, S.V. Vinogradova, and V.A. Vasnjov, *Faserforschung und Textiltechnic*, 28, 491 (1977).
14. V.V. Koršak, *Faserforschung und Textiltechnik*, 28, 561 (1977).
15. V.V. Korshak and S.V. Vinogradova, *Non-equilibrium Polycondensation*, Moscow, Nauka, 1972 (in Russian).
16. V.V. Korshak, *Raznozvennost' of Polymers*, Moscow, Nauka, 1977, p. 22-76 (in Russian).
17. V.V. Korshak, *Usp. Khimii*, 49, No. 12, 2286 (1980).
18. V.V. Korshak, *Vysokomolek. Soed.*, 21A, 4 (1979).
19. V.V. Korshak, *Raznozvennost' of Polymers*, Moscow, Nauka, 1977, p. 190 (in Russian).
20. V.V. Korshak, N.M. Kozyreva, G.N. Menchikova, A.V. Gorshkova, E.A. Grigoryan, and F.S. D'yachkovsky, *Vysokomolek. Soed.*, 21A, 144 (1979).
21. V.V. Korshak, N.M. Kozyreva, G.N. Menchikova, A.V. Gorshkova, E.A. Grigoryan, and F.S. D'yachkovsky, *Dokl. Akad. Nauk SSSR*, 246, 372 (1979).
22. V.V. Korshak, N.M. Kozyreva, S.B. Skubina, F.S. D'yachkovsky, B.I. Tsytkova, and P.M. Nedorezova, *Vysokomolek. Soed.*, 23A, 2788 (1981).
23. B.V. Lebedev, N.N. Smirnova, N.K. Lebedev, N.M. Kozyreva, A.I. Kirilin, and V.V. Korshak, *Dokl. Akad. Nauk SSSR*, 270, 129 (1983).
24. N.M. Kozyreva, A.I. Kirilin, A.V. Gorshkova, and A.A. Askadsky, *XII Mendeleev Congress on General and Applied Chemistry, Abstracts of Papers*, Issue 2, Moscow, Nauka, 1981, p. 217.
25. V.V. Korshak, N.I. Bekasova, V.V. Vagin, and A.A. Izyneev, *Dokl. Akad. Nauk SSSR*, 210, 110 (1973).
26. V.V. Korshak, *Thermally Stable Polymers*, Moscow, Nauka, 1969 (in Russian). 27
27. B.Ke, *J. Polymer Sci.*, 42, 47 (1960).
28. V.V. Korshak, *Raznozvennost' of Polymers*, Moscow, Nauka, 1977, pp. 156-185 (in Russian).
29. V.V. Korshak, *Raznozvennost' of Polymers*, Moscow, Nauka, 1977, pp. 81-136 (in Russian).
30. Karl-Heins Illers, *Ber. Bunsenges., Phys. Chem.*, 70, 353 (1966).
31. V.V. Korshak and T.M. Frunze, *Izv. Akad. Nauk SSSR, OKhN*, 163, 551 (1955); 98 (1956).
32. K.-H. Illers, *Ber. Bunsenges., Phys. Chem.*, 70, 3 (1966).
33. L.A. Wall, S.L. Madorsky, D.W. Brown, S. Straus, and R. Simha, *J. Amer. Chem. Soc.*, 76, 3430 (1954).
34. K.G. Grigor'ev, V.A. Sergeev, V.K. Shitikov, and V.V. Korshak, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1488 (1973).
35. G.P. Belonovskaya, S.E. Bresler, B.A. Dolgoplosk, A.T. Os'minskaya, and A.G. Popov, *Dokl. Akad. Nauk SSSR*, 128, 1179 (1959).
36. V.V. Korshak, G.L. Berestneva, and I.P. Bragina, *Vysokomolek. Soed.*, 14A, 1036 (1972).
37. V.V. Korshak, Yu.E. Doroshenko, V.A. Khomutov, and R.D. Katsarava, *Dokl. Akad. Nauk SSSR*, 200, 1361 (1971).
38. V.V. Korshak, L.S. Fedorova, K.K. Mozgova, and N.A. Satskaya, *Vysokomolek. Soed.*, 11A, 43 (1969).

3 Progress in Polycondensation

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1. INTRODUCTION

Polycondensation is the most important method of synthesis of high-molecular compounds. During 150 years since the synthesis of the first polymer by polycondensation [1] the method has received comprehensive development from the viewpoint of understanding the general regularities of polymer formation and also in relation to its use in the synthesis of a large number of polymers of different types: phenol- and melamine-formaldehyde resins, alkyd resins, linear polyethers and polyesters, polyamides, polymers of cyclochain structure, polyorganosiloxanes, polyorganoelementsiloxanes, coordination polymers, etc. Many of these polymers are being manufactured on a commercial or experimental scale and find wide application.

Thus, polycondensation opens up broad fields of preparing polymers of various chemical structure and hence with highly diversified properties including elevated thermal and heat resistance, electrical conductivity, favourable insulating properties and mechanical parameters, light sensitivity, physiological activity, etc.

In the USSR studies in the field of polycondensation started developing mostly from the 1930s-1940s although it is worth mentioning that as early as in 1859 Butlerov [2] obtained polyformaldehyde by polycondensation of methylene iodide with silver oxide, Menshutkin [3] in 1881 studied the kinetics of ethylene glycol polyesterification with succinic acid, and in 1912 Petrov [4] organized commercial production of phenol-formaldehyde polymers.

During the last 50 years polycondensation has been developed and has shaped up as an independent section of chemistry of high-molecular compounds, as was indicated in many monographs and reviews some of which are given in the list of references [5-29].

2. EQUILIBRIUM AND NON-EQUILIBRIUM POLYCONDENSATION

'Polycondensation' is used to denote the processes of polymer formation based on elementary substitution reactions [30]. This is its principal difference from polymerization based on addition reactions. Unlike polymerization based mainly on two

chemical processes: addition to multiple bonds between two atoms and addition to cycles, polycondensation processes are varied because both organic and inorganic chemistry know many different substitution reactions that at present are being successfully used for preparing organic, organoelement, and inorganic polymers [8, 9, 18, 19, 25, 27].

Investigation of the polycondensation regularities and the generalization of extensive experimental data led to an idea that the known polycondensation processes can be subdivided into two groups: equilibrium and non-equilibrium polycondensation [8, 9, 28, 31, 32] differing in the character of the main reactions and the equilibrium constant.

The main feature of non-equilibrium polycondensation is the absence of polymer destruction by the lowmolecular polycondensation product:

$$x\ \mathrm{a{-}A{-}a} + x\ \mathrm{b{-}B{-}b} \rightarrow (\mathrm{{-}A{-}B{-}})_n + 2x\ \mathrm{ab}$$

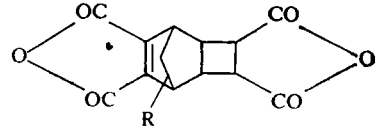
and also in most cases the absence of other exchange destructive transformations in the polycondensation process. Therefore, non-equilibrium polycondensation is characterized by the high equilibrium constant values, i.e. the rate of the forward reaction (the formation of the macromolecule) should be significantly higher than the rate of the reverse destructive reaction. It has been proposed to class arbitrarily the reactions with an equilibrium constant not exceeding 10^3 with equilibrium polycondensation [20, 33].

For such classic cases of equilibrium polycondensation as polyesterification and polyamidation, the equilibrium constant accounts for some unities. The polycoordination equilibrium constant has the same order of magnitude [19, 20]. On the other hand, in the case of non-equilibrium polyesterification, the equilibrium constant exceeds 10^3, for low temperature formation of polyamido acids it is larger than 10^5 litre/mole, for the formation of polyaminoamido acids it equals 7×10^{21}-5×10^{28} litre/mole [19, 34, 35].

The value of the equilibrium constant depends not only on the reaction type, it can also be strongly affected by the chemical structure of the initial substances in the same transformation type, as can be seen from Table 1 containing equilibrium constants of formation of polyamido acids based on the acid dianhydrides of different structure in dimethyl formamide at 25 °C [36]. It was also found that the equilibrium constant of this reaction depends on the diamine structure and diminishes in the following series: *p*-phenylenediamine > *m*-phenylenediamine > diaminodiphenylethane > diaminodiphenylmethane > diaminodiphenyl sulphide > diaminodiphenyl sulphone [36].

The equilibrium constants of polycondensation can be influenced by the reaction temperature and medium, as is shown in Table 2.

Table 1. Equilibrium Constants and Rate Constants of Interaction of 4,4′-Diaminodiphenylethane with Acid Dianhydrides,



R in the dianhydride	Equilibrium constant	$k_1 \times 10^2$	$k_2 \times 10^3$
		litre·mole^{-1}·s^{-1}	
—H	807	2.64	4.10
—Cl	6600	4.81	27.80
—$C(CH_3)_2$	139	2.41	0.79
—$CH_2CH(CH_3)_2$	121	3.26	1.44
—$CH(CH_3)_2$	274	3.14	1.86

For strongly differing activation energies of the forward and back reactions the process at certain temperatures can be an equilibrium one whereas at other temperatures, non-equilibrium (Table 2).

Table 2. Dependence of Equilibrium Constant K on Temperature and Solvent for Model Interaction between Phthalic Anhydride and Aniline [35, 37]

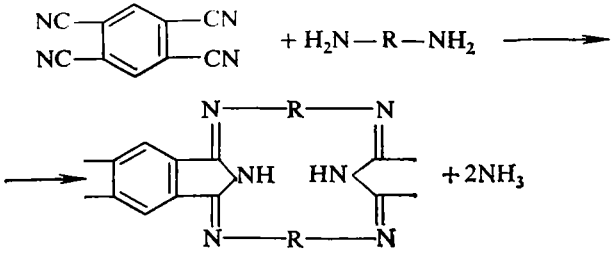
T, °C	K, litre/mole, in acetonitrile	K, litre/mole, in tetrahydrofuran
40*	1970	17 600
100	110	600
150	17	74
200	4	11
250	1	4

* At 40 °C, K is 2550 in methylethyl ketone and 10^5 litre/mole in dimethylacetamide.

The equilibrium constant of the formation of polyimide from a dianhydride, 3,3′,4,4′-tetracarboxydiphenyloxide and anilinefluorene in N-methylpyrrolidone varies at different temperatures as follows [38]:

T, °C	115	135	150	165
K	5.3×10^4	1.5×10^4	6.6×10^3	3.1×10^3

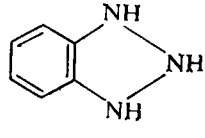
Recent decade has brought about the development of rather complicated polycondensation processes, such as polycondensation of dianhydrides of tetracarboxylic acids with diamines leading in some cases to polymers with macroheterocycles in the chain called polyhexazocyclanes [39, 40]:



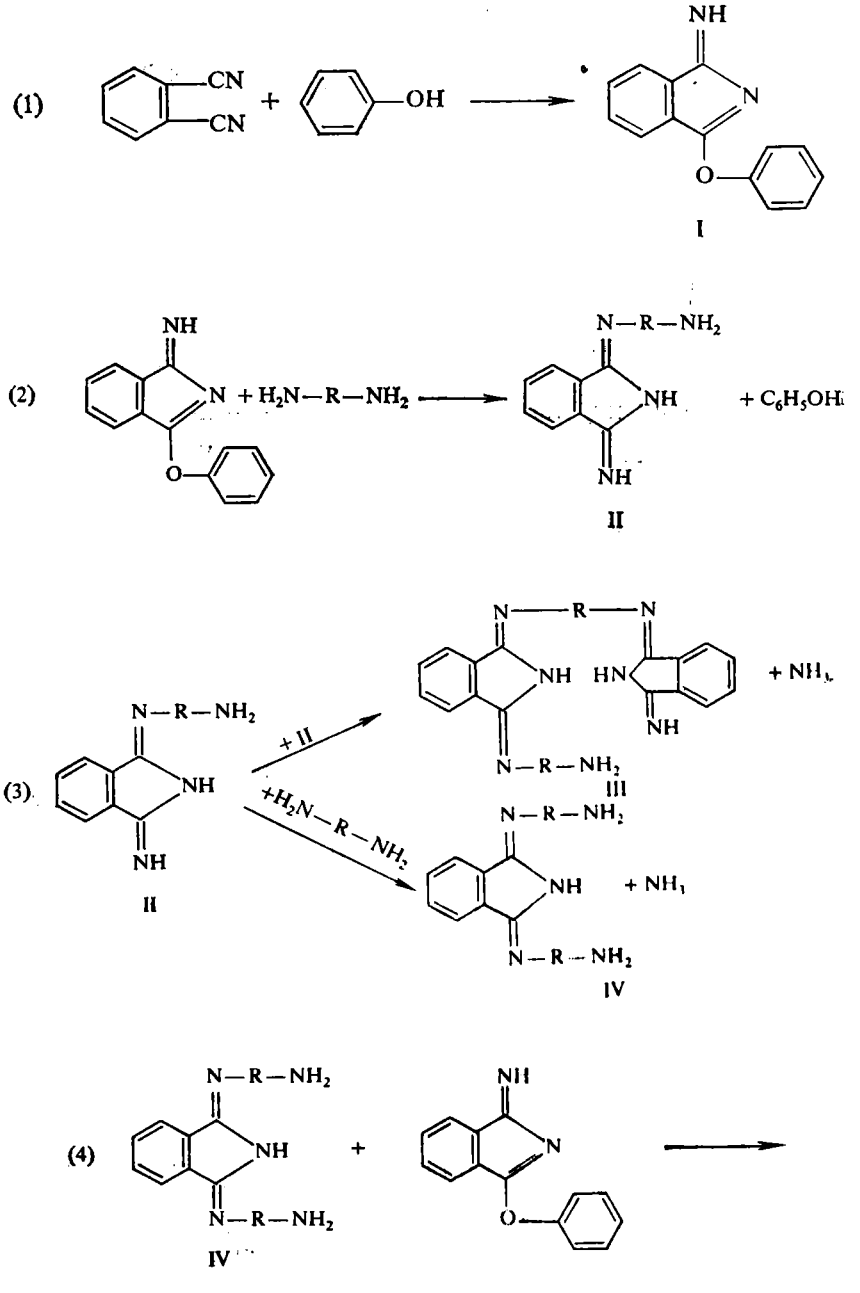
The equilibrium constant values for the model reaction of this type, condensation of phthalodinitrile with *m*-phenylenediamine in phenol are given below [41]:

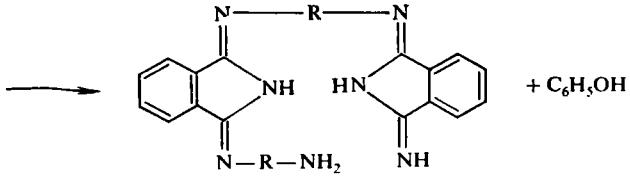
T, °C	147	167	187	207	227
K	9.3×10^{5}	2.2×10^{5}	5.9×10^{4}	1.7×10^{4}	5.3×10^{3}

These figures show that equilibrium constants markedly depend on temperature.

A detailed study of this reaction showed that it is a complex process [42, 43, 44] including several stages presented in Scheme 1. All the reactions proceeding with ammonia evolution are reversible, as evidenced by the fact that the reaction of macroheterocycle V with ammonia gives compounds II-IV and also diamine and 1,3-diimidoisoindoline,  . Compound I is not formed in aminolysis. Reactions (1) and (2) are irreversible because it was found that the keeping of compound II in phenol caused no diamine liberation. This gives grounds to presume that the process of the formation of polyhexazocyclanes by polycondensation of dinitriles of aromatic tetracarboxylic acids with diamines includes reactions both of equilibrium and non-equilibrium type. The equilibrium constants of the process are rather high even at elevated temperatures, which makes one believe that the overall contribution of non-equilibrium steps is substantial. However, the equilibrium stages proceeding with ammonia evolution are also to be taken into consideration to optimize the process of polyhexazocyclane formation.

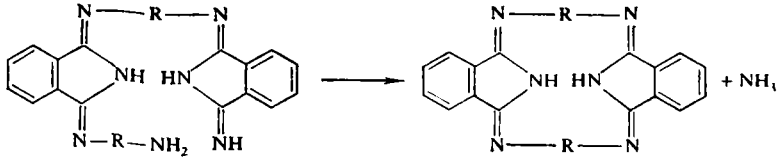
Scheme 1


(1)
CN
CN
+
OH
NH
N
O
I
(2)
NH
N
+ H2N—R—NH2
O
N—R—NH2
NH
NH
+ C6H5OH
II
(3)
N—R—NH2
NH
NH
II
+ II
+ H2N—R—NH2
N
R
N
NH
HN
NH
+ NH3
N—R—NH2
III
N—R—NH2
NH
+ NH3
N—R—NH2
IV
(4)
N—R—NH2
NH
N—R—NH2
IV
+
NH
N
O



III

(5)



III V

frequently, by both simultaneously. This fact in combination with the use of highly reactive initial substances and/or special activators as well as of specific reaction media opens the way to a substantial intensification of polymer synthesis by this method, offers possibilities of running the process under comparatively mild conditions in a very short time.

Even at this stage of progress in non-equilibrium polycondensation intensive study of a number of such processes has already enabled the synthesis of polymers with very high molecular weight attaining tens of thousands and sometimes hundreds of thousands. There is no doubt, however, that many non-equilibrium polycondensation processes will be implemented only in future.

An undoubtful advantage of some non-equilibrium polycondensation processes consists in the fact that they can be run successfully in solution. This, among other things, opened up possibilities of obtaining polymers with high melting points and melt viscosity, i.e. most of polymers with high thermal and heat resistance known at the present time. Also, because of the absence of exchange destructive transformations in the process, non-equilibrium polycondensation will enable, with proper knowledge of corresponding regularities, a purposeful synthesis of copolymers with a desired structure, e.g. block and regularly alternating copolymers.

Finally, yet another very essential feature of these processes. Non-equilibrium polycondensation is highly versatile offering a variety of possibilities both in the sense of the involvement of a broader range of substances of different chemical structure and in the sense of the diversity of the chemical structures of polymers produced by this method [9, 13-15, 17, 19-22, 25]. However, non-equilibrium polycondensation, its main regularities are at present less deeply understood than equilibrium polycondensation [25] and this, of course, puts forward the task of a thorough investigation into these processes.

3. THE EFFECT OF THE STRUCTURE OF THE INITIAL SUBSTANCES

The effective course of polycondensation depends to a great extent on the structure of the initial substances: their functionality, reactivity, and ability to resist side reactions. The views on the substances used as monomers in polycondensation and on the effect of their functionality on the structure of macromolecules have undergone substantial changes during recent decade, mostly because of the progress in non-equilibrium polycondensation [9, 19, 25, 45-48].

Owing to the discovery and use of such non-equilibrium processes as polyrecombination and dehydropolycondensation, the pos-

sibility has arisen of obtaining polycondensation polymers from substances having no "classic" functional groups (NH_2, OH, COOH, etc.) in their molecules. Thus, polyrecombination is being successfully used in producing polymers from alkyl aromatic hydrocarbons, organoelement compounds, etc. [9, 49, 50].

The functionality of monomers is one of the basic concepts in polycondensation [5-9, 14-17, 19, 20, 23, 45-48, 51-56]. Usually this term is understood as the total number of functional groups in the initial substance. Since Carothers' time [54] it was believed that only bifunctional substances could form linear macromolecules by polycondensation; monofunctional compounds do not yield polymers while polycondensation of tri- and higher functional substances led to the formation of branched and cross-linked polymers. The development of the theory and practice of non-equilibrium polycondensation processes made essential corrections for these conceptions; in this respect, much has been done in recent papers of Korshak [23, 25, 46-48] who generalized and formulated the concepts of functionality in polycondensation processes and ascertained the limitedness of the functionality rule advanced by Carothers.

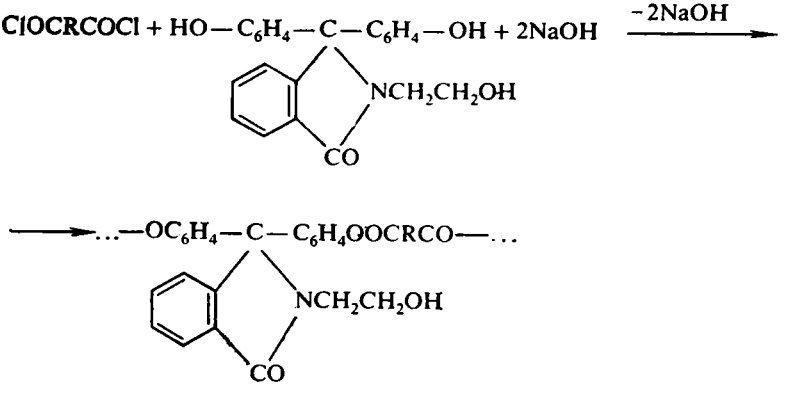
It was proposed to employ three types of functionality: the possible (F_p) which is the overall number of functional groups of all types in the monomer or oligomer, the realizable (F_r) which is the number of functional groups capable of reacting under given conditions, and the relative (F_{rel}) which is equal to the F_p/F_r ratio. In relation to their behaviour in polycondensation, monomers can be divided into two groups: "normal" with $F_p = F_r$ and $F_{rel} = 1$ and "anomalous" with $F_p \geqslant F_r$ and $F_{rel} \geqslant 1$. The formation of linear polymers is possible if at a certain reaction stage $F_r = 2$ and that of three-dimensional polymers if $F_r \geqslant 3$ [46]. The spreading of the functionality concept to oligomers and polymers made it possible to visualize the course of the polycondensation process at its different stages by describing the variation of the functionalities of different types and of the ratios between them [46-48, 57].

The fact that certain monomers with functionality exceeding two form linear, rather than three-dimensional polymers in polycondensation is caused by their specific chemical structure and the reaction conditions.

For instance, in interfacial polycondensation performed under mild temperature conditions, sebacoyl chloride reacts with 1,3-diaminopropanol-2 to give a fusible and soluble polyamide containing free hydroxyls in its chain because of a substantial difference in the reactivities of the amino and hydroxyl groups [59].

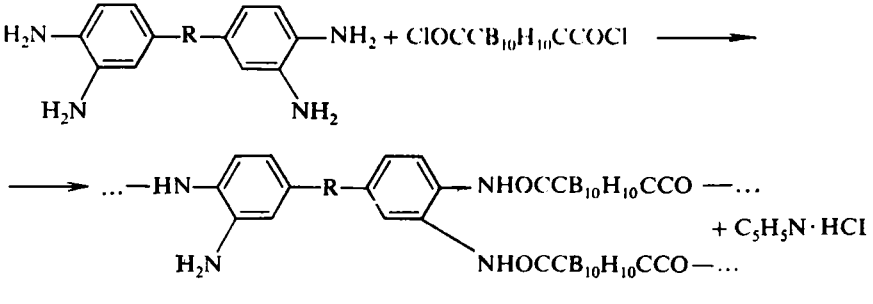
Interfacial polycondensation of such trifunctional substances as 2 β-hydroxyethyl-3,3-bis(4-hydroxyphenyl)phthalimidine or phenolphthalein imide with dicarboxylic acid chlorides yields linear

high molecular polyarylates containing in their chain free hydroxyl or >NH groups [19] which do not react with acid chloride groups under the conditions of the reaction:

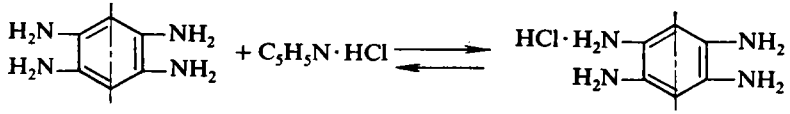


The use of such bisphenols in a mixture with ordinary bisphenols in the synthesis of polyarylates permits a precise control of the above-mentioned reactive groups in the chain because the trifunctional monomers used in these processes act as bifunctional substances due to the substantial difference in $-C_6H_4OH$ and $-CH_2CH_2OH$ (or NH) group reactivity.

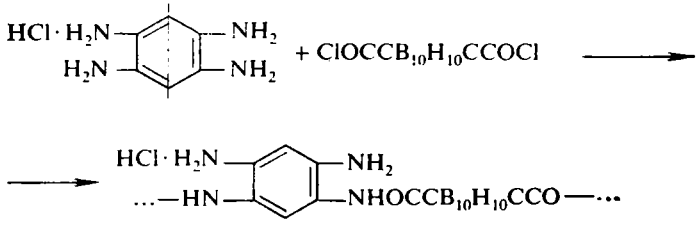
Essential difference in the reactivity of functional groups can arise during the reaction, making part of them unreactive and decreasing thereby the possible functionality. For example, the comprehensive investigation of non-equilibrium polycondensation of *m*- and *p*-carborane dicarboxylic acid chlorides with aromatic tetramines [59, 60] showed that if this reaction is carried out in pyridine, insoluble cross-linked polymers are formed very quickly (2-5 min) since three amino groups of the tetramine react with the acid chloride:



If, on the other hand, pyridine hydrochloride is introduced into the reaction medium, then tetramine hydrochloride is formed at first:



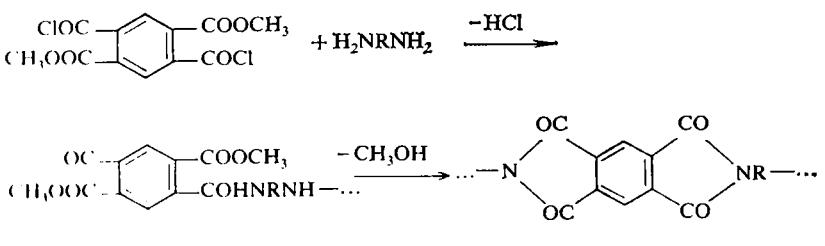
Substantial difference in the reactivities of the free and protonated amino groups of the tetramine and the fact that under the reaction conditions the fourth amino group is not acylated are responsible for selective acylation of the free amino groups and the formation of linear polymers:



Since the reaction of the tetramine with pyridine hydrochloride is an equilibrium process, the equilibrium shift depends on the amount of pyridine hydrochloride; by varying the quantity of pyridine hydrochloride one can control the reactivity of the amino groups in tetramines and to obtain, as a result, the polymers of a desired structure (linear, branched or cross-linked).

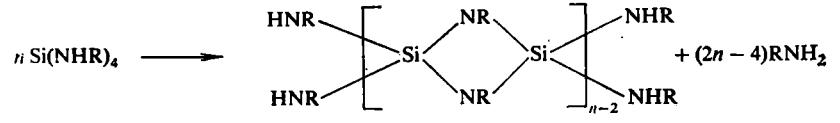
The reactivity of 3,3′-diamino-4,4′-dihydroxydiphenylmethane in its reaction with carborane dicarboxylic acid chloride [61] can be regulated by tributylamine in whose presence a linear polymer is formed; thus, in this case the tetrafunctional initial component acts as a bifunctional monomer.

The functionality of the initial substances in polycyclization reactions is manifested in a peculiar manner. In many cases of polycyclization leading to polyheteroarylenes [9, 62-65] tetrafunctional reactants (aromatic tetramines, dihydroxydiamines, dianhydrides, and other derivatives of tetracarboxylic acids, dithiodiamines, etc.) react at the first reaction stage as bifunctional compounds, realizing their functionality completely only at the second reaction stage:



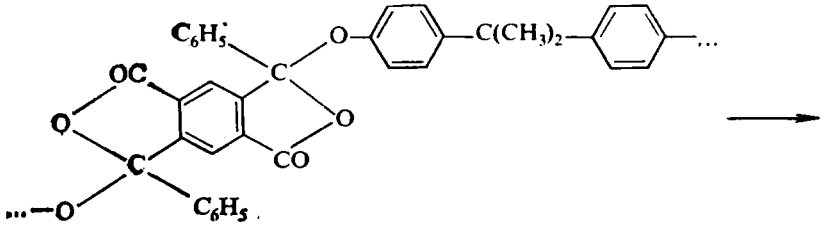
This is caused by favourable arrangement of the functional groups in *ortho* position in these monomers (the term "*ortho* effect" was proposed [46]) allowing for the formation of five- or six-membered cycles during the macromolecule formation. In this case, when the process is carried out under adequate conditions, linear cyclochain polymers are formed, rather than branched or three-dimensional macromolecules, as it could have been expected on the basis of the initial functionalities of the monomers.

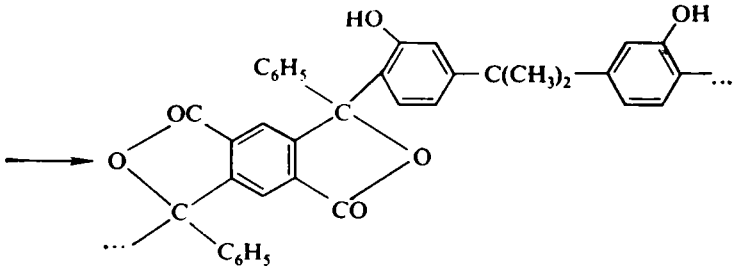
Linear cyclochain polymers can also be formed from tetrafunctional monomers in the case of the spiro structure formation, as is exemplified by tetraalkylaminosilane polycondensation [66]:



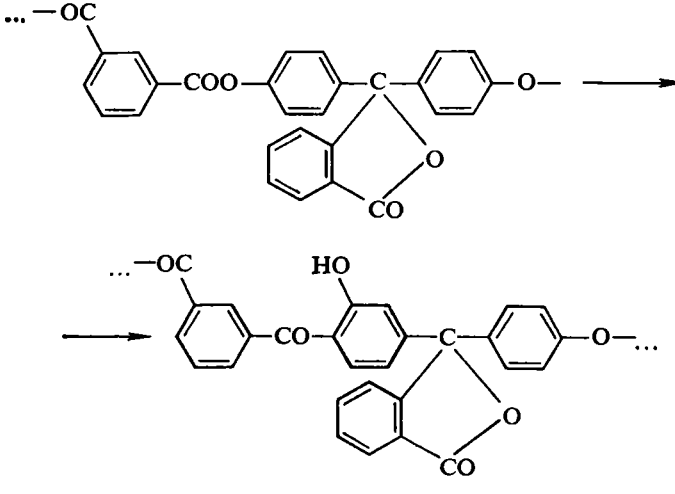
Yet another aspect of functionality in polycondensation should be discussed. In many cases of polycondensation (particularly in the formation of heterochain polymers) the content of the initial free functional groups decreases due to reaction acts but the functionality of the resulting macromolecule progressively increases as its molecular weight grows [47, 49]. This is one of the specific features of polycondensation distinguishing it from polymerization; it results from the fact that new bonds, particularly heterobonds (ester, amide, coordination bond, etc.), under certain conditions are also reactive to "secondary" transformations (acidolysis, alcoholysis, amidolysis, esterolysis, etc.).

Cases are known when new functional groups can arise in the macromolecules also as a result of specific rearrangements. For example, it was found that aromatic polyethers containing phenoxyphthalide fragments [67] undergo rearrangement into polyarylenes with free hydroxyls at the aromatic rings on thermal treatment at 200-300 °C and in the presence of catalysts at lower temperature (25-100 °C) [68]:





The heating (in the presence of catalysts) or UV irradiation of polyarylates of aromatic dicarboxylic acids and bisphenols induces Fries' rearrangement [9, 69, 70] leading to the conversion of ester bonds into keto groups and the formation of free hydroxyl groups at the aromatic rings in the *ortho* position to the keto groups:

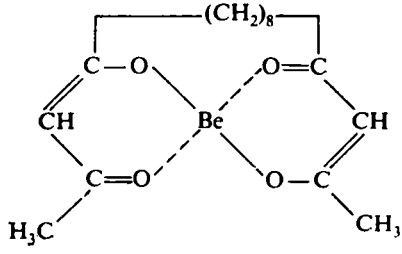


The above data emphasize the importance of the functionality concept in polycondensation and great significance of the functionality realizable in polymer synthesis; skilful control of functionality is also needed for the optimization of polycondensation processes and a purposeful creation of polymers of desired structure and hence with the required set of properties.

Another important feature of the monomer structure strongly affecting the success in polycondensation is their ability of the formation of cyclic low-molecular products [8, 9]. If the number of atoms in the basic unit of the polymer is five, six, and seven, then there arises danger of the formation of low-molecular cyclic products together with the polymer molecule. The possibility of formation of such cy-

cles and even more numerous cycles becomes greater in some non equilibrium polycondensation processes because of the use of very dilute solutions, e.g. in interfacial polycondensation and low-temperature polycondensation in solution [9].

An interesting example of the formation of macrocyclic compounds was disclosed for coordination polymers of bis-β-diketones with beryllium [8, 71-73]. It turned out that these polymers in dilute solutions enter unusually easily into exchange reactions to give cyclic products even at low temperatures. For instance, a macrocyclic monomer complex of sebacyldiacetone and beryllium



was isolated from dilute solutions of beryllium polysebacylacetonate in organic solvents with a 50% yield. These data suggest that polycoordination in not very concentrated solutions involves both polymer chain growth through polycoordination and the destructive process by way of transformation of the coordination polymer into cyclic products. There is every reason to believe that any heterochain polymer in dilute solutions under the conditions enabling exchange reactions between the polymer chain units can undergo degradation to give macrocyclic compounds:

$$(-A-B-)_x \rightleftharpoons \frac{x}{k+n} \begin{bmatrix} -(A-B)_k- \\ -(B-A)_n- \end{bmatrix}$$

The size of the cycles formed in this process is likely to be determined both by thermodynamic and energetic factors. From the thermodynamic viewpoints, the size of the cycles should be the smallest since the entropy of the system in this case will be the highest. On the other hand, the formation of less strained cycles is energetically more advantageous and the size of the cycles as well as the possibility of their formation will depend on the structure of the polymer and hence on the structure of the initial substances. Thus, in some polycondensation processes the possibility of such a competing side reaction as cyclization should be taken into account.

In the course of polycondensation, the initial monomers and polymer chains can lose their reactive functional groups in a number of other chemical side transformations as well: decarboxylation, hydrolysis, complexing, etc. [8, 9]. The facility of side processes of deactivation of functional groups depends both on the polycondensation conditions and on the chemical structure of the monomer. The finding of the ways of preventing side reactions of this type is undoubtedly one of the paramount prerequisites of success in carrying out polycondensation.

4. THE STAGES OF MACROMOLECULE GROWTH IN POLYCONDENSATION

The polymer chain formation during polycondensation can be formally subdivided into three stages: start of chain propagation, chain growth, and chain termination, each of the stages featuring the formation of a stable compound capable of independent existence. A low-molecular polycondensation product is liberated simultaneously with chain growth.

4.1. Start of Chain Growth

Start of chain growth in polycondensation can most often be represented by the following schemes [19, 24]:

1. The elementary act consists in formation of the intermediate active state on the collision of two functional groups:

$$a—A—a + b—B—b \rightarrow a—A—a\cdot b—B—b$$

which decomposes with the formation of a new bond and the liberation of a low-molecular polycondensation product:

$$a—A—a\cdot b—B—b \rightarrow a—A—B—b + ab$$

2. The intermediate active state resulting from interaction of the third substance (not participating in the build-up of the polymer chain) with one of the initial substances:

$$a—A—a + C \rightarrow a—A—a\cdot C$$

$$b—B—b + C \rightarrow b—B—b\cdot C$$

which easily reacts with the second initial component and regenerates the third substance:

$$a—A—a\cdot C + b—B—b \rightarrow a—A—B—b + ab + C$$

$$b—B—b\cdot C + a—A—a \rightarrow b—B—A—a + ba + C$$

or forms the product of binding the latter with the low molecular polycondensation product: ab·C. Another possibility involves the formation of adducts between the two initial substances and the in-

termediate active substance; further reaction occurs between these two intermediate molecules:

$$a—A—a\cdot C + b—B—b\cdot C \rightarrow a—A—B—b + ab + 2C$$

3. The first stage of the reaction consists in the dissociation of one of the reactants into ions:

$$a—A—a \rightarrow {}^{+}A—a + a^{-}$$

reacting with the second reactant:

$${}^{+}A—a + b—B—b \rightarrow a—A—B—b + {}^{+}b,$$

$$a^{-} + {}^{+}b \rightarrow ab$$

or both monomers dissociate into ions:

$$a—A—a \rightarrow a^{-} + {}^{+}A—a$$

$$b—B—b \rightarrow {}^{+}b + {}^{-}B—b$$

followed by the reaction:

$${}^{+}A—a + {}^{-}B—b \rightarrow a—A—B—b$$

$$a^{-} + {}^{+}b \rightarrow ab$$

4. The active particles involved in the construction of the polymer chain are free radicals produced by decomposition of an active compound, e.g. organic peroxide: $C \rightarrow C\cdot$; the active particles induce homolytical detachment of labile atoms from the monomer molecule:

$$a—A—a + C \rightarrow a—A\cdot + aC$$

The radicals so formed recombine to form the dimer:

$$a—A\cdot + a—A\cdot \rightarrow a—A—A—a$$

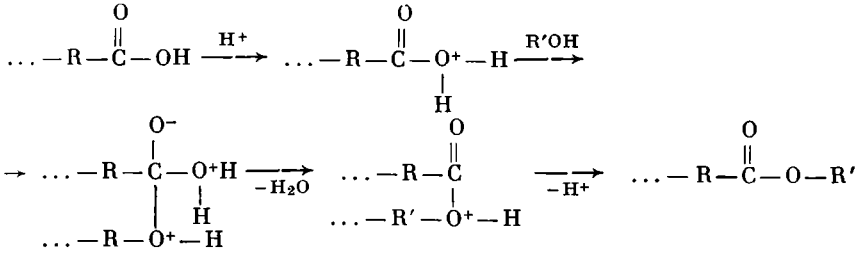
Subsequent elementary reaction steps occur between the functional groups similarly.

Based on the fact that all ionic polycondensation processes involve the formation of ions and ionic systems, it was proposed to class these processes into three groups [24, 74, 75]: cationic polycondensation, anionic polycondensation, and ionic coordinate polycondensation. Polycondensation whose elementary acts are associated with the formation of free radicals belongs to free-radical polycondensation.

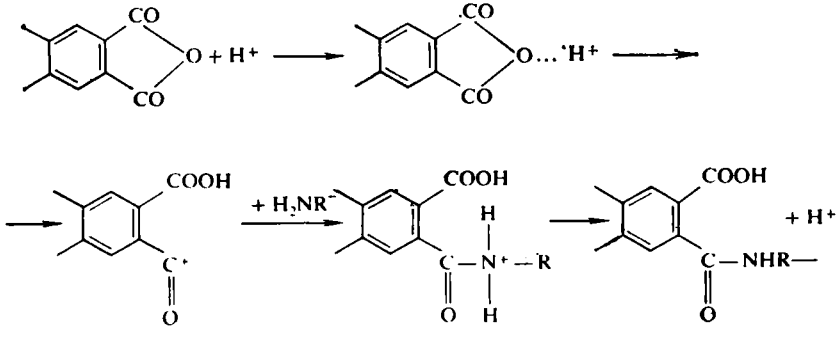
Unfortunately, only relatively few polycondensation processes have been studied in detail, including the knowledge of the mechanism of the individual reaction stages. However, an idea of the mechanism of elementary acts can be obtained from the kinetic data, model reactions, and general concepts of organic chemistry. Below are discussed some examples of the course of the elementary act by different mechanisms.

Thus, there is good reason to believe that equilibrium polyesterification in the presence of acid catalysts involves the cationic

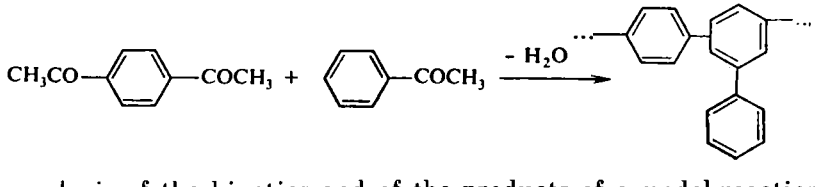
mechanism [24]:



Studies of the kinetics of polyamido acid formation showed that this reaction between cyclic tetracarboxylic acid anhydrides and aromatic diamines has autocatalytic character due to carboxylic group formation during the anhydride cycle opening. A catalytic method of polyamido acid preparation in the presence of carboxylic acids has been elaborated on this basis [76-78]. It is believed that this interaction proceeds by the cationic mechanism:



Polycyclocondensation of acetylaromatic compounds, which is being successfully developed at present and gives rise to polyphenylenes [79-87], belongs to new interesting and peculiar cases of non-equilibrium polycondensation. Diketones, ketals, and a mixture of mono- and diacetyl derivatives are used in this reaction:



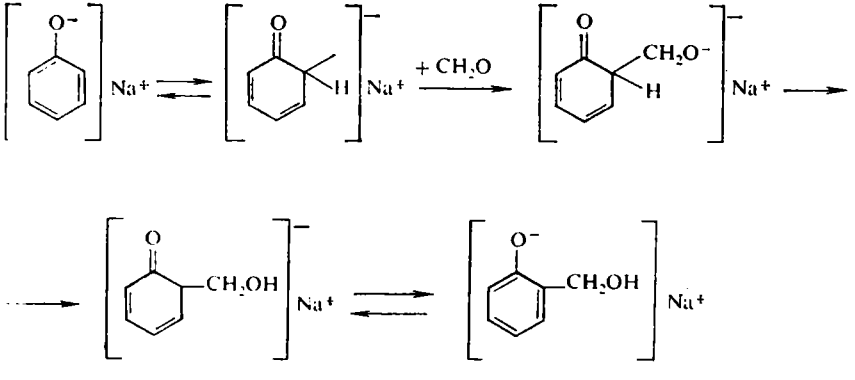
An analysis of the kinetics and of the products of a model reaction, a comparison of the published data concerning the mechanism of croton condensation and the properties of ketals provided an idea of

the mechanism of the process. The first stage of the reaction in the presence of acid catalysts (e.g. hydrogen chloride) is the addition of proton to the ketal with formation of a carbocation. Therefore, this reaction type can be placed in the category of polycondensation processes governed by the cationic mechanism.

Starting from the 1960s, a number of studies have been carried out in the field of kinetics and mechanism of polycondensation of dicarboxylic acid chlorides with bisphenols in solution on heating; this reaction affords heat-resistant polymers called polyarylates which are of interest from the practical viewpoint [9, 12, 88-98]. The interaction between terephthaloyl chloride and 9,9-bis(4-hydroxyphenyl)fluorene or 4,4′-(hexahydro-4,7-methyleneindan-5-ylidene)-diphenol [82, 86] carried out under conditions typical of preparation of polyarylates by high temperature polycondensation (150-200 °C, in ditolylmethane, dinyl or nitrobenzene) has been studied in detail. According to the initial reaction rates, the order of reaction is 1.5, i.e. the first order with respect to the bisphenol and 0.5 with respect to the acid chloride. An analysis of the kinetic data and the results of the measurement of the electrical conductivity of the system showed that the reaction follows the ionic mechanism. The first stage is equilibrium ionization of one of the acid chloride groups. The resulting acylium ion reacts with the phenol or recombines with the chloride ion. The second stage is equilibrium ionization of the acid chloride group in the ester acid chloride followed by reaction with the phenol.

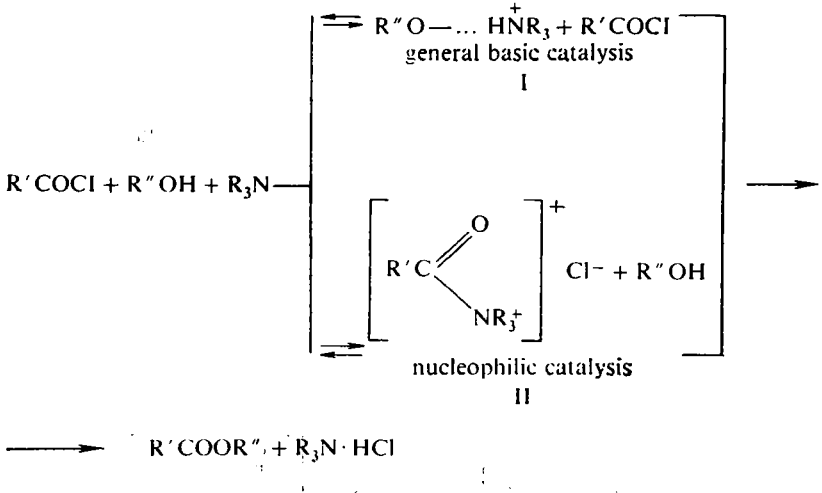
The above-mentioned results indicate that dicarboxylic acid chlorides can react with bisphenols by the ionic mechanism. On the other hand, it has been reported in a number of papers that the reaction of dicarboxylic acid chlorides with bisphenols is a second order reaction [9, 92, 94, 96-98].

The ionic mechanism of polycondensation can be exemplified by interaction of phenols with aldehydes in the presence of alkaline catalysts [99]:



Acceptor-catalytic polyesterification of dicarboxylic acid chlorides with bisphenols in the presence of tertiary amines has received much attention in recent studies; this process obeys the ion-coordinated mechanism [9, 19, 22, 100-105]. Detailed study of the initial stage of acceptor-catalytic acylation performed by PMR, NQR, IR, and UV spectroscopy, potentiometry methods, investigation of the kinetics of model reactions of phenols with aromatic dicarboxylic acid chlorides, determination of the relative reactivity of phenol and substituted phenols in reactions with benzoyl chloride (competitive acylation) in the presence of tertiary amines, and other studies made it possible to establish the mechanism of the elementary acts in the process of acceptor-catalytic polyesterification. It was found that depending on the structure of the reactants and on the process conditions, acceptor-catalytic polyesterification proceeds by the mechanism of general basic or nucleophilic catalysis involving the formation of intermediate complexes of tertiary amines with phenols or acid halides (Scheme 2).

Scheme 2



In the absence of steric hindrances at the reaction centre, increase in the acidity of the diol or in the basicity of the tertiary amine provides conditions for polyesterification to occur by the general basic catalysis mechanism. In accordance with the dual mechanism of acceptor-catalytic polyesterification, the reactivity of diols depends not only on their acid-base properties but also on the basicity of the tertiary amine. Since an increase in the basicity of the tertiary amine increases the contribution of general basic catalysis, more acidic diols (bisphenols) are more active than less acidic ones (glycols) in the presence of strongly basic tertiary amines (trialkyl-

amines). In the presence of weakly basic tertiary amines (e.g. heterocyclic tertiary amines) when the contribution of nucleophilic catalysis increases, the dependence of the reactivity of diols on their acid-base properties is reversed; glycols are more reactive than bisphenols. Nucleophilic catalysis is possible under the following conditions: (1) the tertiary amine is more basic than the leaving group in R'COX; (2) the nucleophile, R"OH, attacking the acylammonium complex is more basic than the leaving ammonium ion [69].

The interaction between aromatic amines and the carboxylic acid derivatives was found to be of an electron-acceptor character; it was demonstrated that the acylation reaction underlying the synthesis of aromatic polyamides and corresponding prepolymers for polyheteroarylenes follows the scheme: reactants $\rightleftarrows$ π-complex $\rightarrow$ $\rightarrow$ δ-complex $\rightarrow$ reaction products, i.e. it proceeds through the intermediate CTC stage [34].

An example of polycondensation in which the elementary act passes through the free radical stage is polyrecombination discovered by Korshak with coworkers [49]. The first stage of this reaction is abstraction of a hydrogen atom from the initial compound with two reactive centres as a result of the attack by an active free radical: $H—R—H + R_1^{\cdot} \rightarrow H—R^{\cdot} + R_1H$. The ability of different hydrocarbons to undergo this type of reactions with homolytical abstraction of hydrogen atoms is determined both by the polar factor affecting the electron density of the C—H bond and the stabilization factor of the radical formed [106].

In considering the elementary acts of the polycondensation process, of importance are the problems associated with the catalysis of these reactions. Despite the fact that in some cases polycondensation can be run in the absence of specially added catalysts, catalysis is of much importance in polycondensation and is extensively used [8, 9]. The general property of the catalysts used in polycondensation is their ability to form intermediate products with the reactants, thus raising their chemical activity.

However, since polycondensation is characterized by great variety of chemical transformations and by the involvement of a large number of functional groups of different types in the reaction [8, 9, 19, 24, 74], the problems of catalysis in this method of synthesis of high-molecular compounds are on the whole very complicated. Unfortunately, till now catalysts are usually selected experimentally.

Diverse acidic (inorganic acids, *p*-toluene sulphonic acid, etc.) and basic catalysts (hydroxides of alkaline and other metals, organic bases), metal oxides, metals (sodium, magnesium, etc.), various salts are broadly used in polyesterification processes [8-11, 24, 74, 75]; phosphoric and boric acids, magnesium oxide, zinc chloride, etc. are employed in polyamidation [11]; Friedel-Crafts type catalysts are utilized in polytransarylation, acylation, and alkylation [8, 24];

various inorganic and organic acids, alkalis, metal oxides, many salts catalyze the interaction of aldehydes with phenols and amides [9, 24, 99]; platinum, copper/ammonia complex, vanadium oxide, etc. are of use in dehydropolycondensation [9, 24]; peroxides, e.g. di-*tert*-butyl peroxide, are applied in processes proceeding by the radical mechanism [9].

The generalization of a great body of experimental data recently made by Korshak [24, 74, 75] has culminated in the separation of catalysts used in polycondensation into three groups in relation to the mechanism of elementary polycondensation acts and with allowance made for the fact that all ionic polycondensation processes involve the formation of ions and ionic systems: (1) catalysts forming reactive cations; (2) catalysts forming reactive anions; (3) catalysts forming reactive salt-like compounds. Korshak analyzed the mechanism of catalyst action in a number of important polycondensation processes and clearly demonstrated the great diversity of catalysts employed in polycondensation processes.

The application of catalysts is undoubtedly reasonable since in their presence polycondensation processes can be run at a higher rate and in milder conditions. However, in some instances the use of catalysts is complicated by the fact that they can stimulate undesirable side processes (the formation of different-unit ('raznozvenny') polymer chain [107], premature chain termination, etc.), impair the properties of the final polymer in articles. To avoid deterioration of the properties special operations aimed at removing the catalyst from the polymer are needed. On the whole, the catalysis problem is very important and urgent for many polycondensation processes and necessitates thorough investigations.

4.2. Macromolecular Chain Growth (Formation)

The chain of the macromolecule in the polycondensation processes grows in a stepwise manner. At first the elementary acts occur predominantly between the functional groups of monomers giving rise to dimers, trimers, and other oligomers. As the monomers are exhausted, reaction between the functional groups of the growing polymer molecules begins to predominate over reaction between the functional groups of the monomers and oligomers, as was shown experimentally [89, 97, 108-110]; at a certain reaction stage the interactions between the chains become the main way of the macromolecule growth. It should be noted here that such a reaction type of the polymer chain growth is typical mostly of polycondensation processes and is one of the signs distinguishing it from polymerization [47, 48]. All elementary acts in the process of growth of the polymer chain proceed through the intermediate state characteristic of this reaction type.

However, in the equilibrium polycondensation and in some cases of non-equilibrium polycondensation, the formation of the macromolecule is not limited to successive acts of growth being more complex. This takes place when the resulting polymer can react not only with the low molecular polycondensation product (in equilibrium polycondensation) but also can enter into exchange interaction with the initial substances and polymer molecules.

Many years of thorough studies of polyesterification, polyamidation, polycoordination, and other types of equilibrium polycondensation carried out at elevated temperatures resulted in the understanding of the mechanism and main regularities of macromolecule formation in these processes and revealed the importance of exchange reactions (hydrolysis, acidolysis, alcoholysis, amidolysis, esterolysis, ketolysis, etc.) concurrent with the main synthetic process and, in combination with the latter, making up a dynamic system of synthetic and destructive reactions, the so-called "polycondensation equilibrium" [5-12].

Sometimes in the process of non-equilibrium polycondensation the resulting polymer, being chemically inert with respect to the low molecular polycondensation product, can take part in exchange reactions with the initial substances and other polymer molecules. This occurs, for example, in polycondensation of aromatic dicarboxylic acid chlorides with bisphenols at elevated temperatures [89, 111, 112]. It is true that the role of destructive processes in this case is slightly limited by the higher stability of the ester linkage in polyarylates to chemical attack in comparison with other heterochain polyesters.

Polymers of cyclochain structure are sometimes also capable of exchange destructive reactions. Thus, examination of the effect of the initial substances or of chemically similar compounds on polyoxadiazoles on heating showed that these polymers are stable to low molecular 1,3,4-oxadiazole, i.e. to exchange reaction between the oxadiazole cycles, but are degraded with hydrazides and acids [113]. Polyimides on heating undergo destructive aminolysis but are stable to acidolysis and exchange reactions involving the imide cycle [114, 115].

From the kinetic viewpoint, polycondensation processes can be divided into two groups [19, 32, 116]. The first group includes non-equilibrium polycondensation reactions proceeding at a high rate under mild conditions (low temperatures). These are e.g. interfacial and low temperature polycondensation in solution. The running of these processes at low temperatures is facilitated by the use of reactants of suitable structure (polycarboxylic acid chlorides and anhydrides) and of efficient catalysts (including catalytically acting solvents) for this type of reactions [9]. The reactions which proceed rather slowly and require elevated temperatures belong to the second

group. Among these reactions are different cases both of equilibrium and non-equilibrium polycondensation, e.g. the formation of a number of polyines by dehydropolycondensation, the synthesis of polyarylenesulphonoxides, polyarylates (from dicarboxylic acid chlorides and bisphenols on heating in high boiling solvents), the preparation of polymers by polycyclization (polybenzimidazoles, polyaminotriazoles, etc.) [8, 9].

The time dependence of the reduced viscosity of polyarylates synthesized by acceptor-catalytic [117] and high temperature [93]

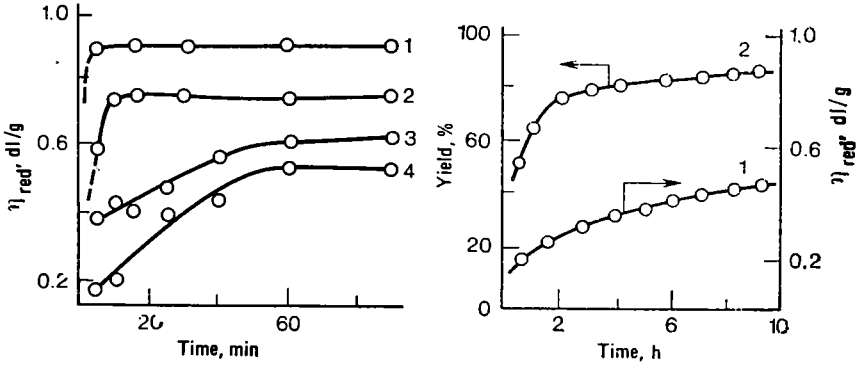


Fig. 1. Variation of the reduced viscosity of a polyarylate solution in tetrachloroethane in the course of acceptor-catalytic polycondensation of terephthaloyl chloride with phenolphthalein in dichloroethane in the presence of triethylamine.

Acid chloride : phenolphthalein: triethylamine molar ratio = 1 : 1 : 2; temperature, °C: (*1*) 50, (*2*) 30, (*3*) 0, (*4*) —20.

Fig. 2. Variation of the reduced viscosity of a polyarylate solution in tricresol (*1*) and of the yield of the polymer (*2*) in the course of polycondensation of isophthaloyl chloride with 4,4′-dihydroxydiphenyl-2,2-propane in dinyl at 220 °C

polyesterification is presented in Figs. 1 and 2 for comparison of the rates of polycondensation processes belonging to the different kinetic groups. In the first case (50 °C) the growth of the molecular weight and also of the yield stops in about five minutes while the synthesis of polyarylate in the absence of tertiary amine (220 °C) takes hours. High rate is peculiar to such a non-equilibrium polycondensation process as low-temperature polyamidation [118-120]. For instance, polycondensation of isophthaloyl chloride with anilinefluorene in dimethyl acetamide at —30 °C was accomplished in several minutes [118].

There are many data on the kinetics of different equilibrium polycondensation reactions [8]. Much less information concerning the kinetics of non-equilibrium polycondensation is available, partic-

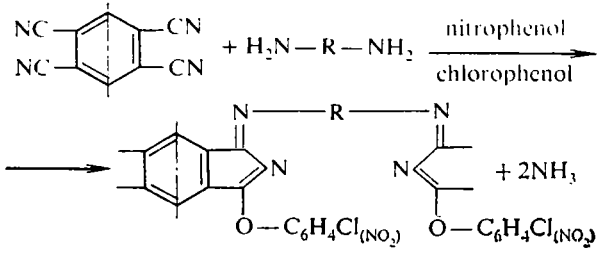
ularly, in the case of high-rate reactions [9]. However, in recent years much emphasis is being placed on the kinetic aspects of various non-equilibrium processes, including model systems [9, 91-98, 113, 121-134].

Information on the kinetics and regularities of the formation of such polymers or model systems as polyarylates [9, 12, 79-89, 102-104], polybenzoxazoles [34], polyoxadiazoles [113, 121-125], polyphenylenes [80], polyhexazocyclanes [43, 44], polyimides [34, 35, 63, 65, 126-130], etc. has appeared in recent decade. The tendency towards extensive use of various spectral, thermochemical, and thermodynamic methods together with the traditional chemical methods can be noted in polycondensation studies [34, 35, 41, 125, 127, 128, 131-134].

From the kinetic standpoint, polyesterification seems to be studied most thoroughly [8, 9]. It has already been said that the kinetics of polycondensation of dicarboxylic acid chlorides with bisphenols at elevated temperatures was studied in a number of experiments [9, 12, 79-89]. The kinetics of acylation of phenols with acid chlorides in the presence of tertiary amines modelling acceptor-catalytic polyesterification was also examined [22, 102-104]. It was shown that the overall order of acceptor-catalytic polyesterification is three (first order with respect to each of the reactants) and that the rate-controlling stage is the interaction of complex I with phenol or complex II with acid chloride, depending on the mechanism of the process (Scheme 2). The rate of acceptor-catalytic polyesterification is greatly affected by the nature of the solvent and by the reaction temperature [22, 105]. It was found that the growth of polarity of the solvent raises the reaction rate. A complex dependence of the rate constant on temperature which does not follow Arrhenius equation was found in a broad temperature range (from —30 to +80 °C); the complexity of the dependence is caused by the reaction mechanism involving a number of stages. An analysis of the effect of temperature on acceptor-catalytic polyesterification [135-141] showed that in the case of highly reactive initial substances in a homogeneous system the temperature dependence of the molecular weight of polyester is depicted by a curve with two maxima evidently because of a polyextremal effect of temperature on the chain growth rate constant [105]. It also turned out that successful growth of the polymer chain in this process is strongly influenced by the nature of the solvent. The aggregation of macromolecules formed as a result of interaction between terephthaloyl chloride and dichlorodian in a metastable solution (e.g. dichloroethane/acetone) creates more favourable conditions for the formation of high-molecular polymers than in a process carried out in a thermodynamically stable solvent having a similar value of the dielectric constant [140]. It appears that such aggregation leads to a local increase in the concentration

of the end groups of the polymer chains; this, on the one hand, raises the macromolecular growth reaction rate and, on the other hand, diminishes the cotribution of side reactions. Generally speaking, the precipitation of the polymer from solution under the conditions of acceptor-catalytic polyesterification does not hamper the further growth of the polymer chain by interaction between macromolecules or between macromolecules and the initial compounds [140, 142, 143]. Optimum conditions of synthesis of polyarylates in a heterogeneous system are high solubility of monomers in the reaction medium, strong swelling ability of the polymer in a low-polarity medium or high polarity of the medium when the swelling ability of the polymer in the solvent is limited [143].

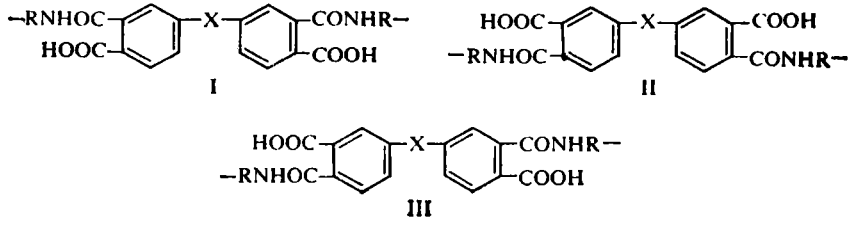
The reaction medium strongly affects the formation of macromolecules in many other polycondensation processes as well. Recent studies of the influence of the reaction medium on the condensation of phthalodinitrile with *p*-phenylenediamine [39, 40] modelling the polycondensation of tetranitriles of tetracarboxylic acids with diamines demonstrated that the reaction medium can have a decisive effect on the result of the reaction. For instance, this reaction in phenol or cresols affords the macroheterocycle as the main reaction product, in aliphatic alcohols the yield of this product does not exceed 30%, and condensation in phenols with electron accepting substituents does not result in the formation of the heterocycle at all but involves only linear condensation. Therefore, if polyhexazocyclanes are to be obtained, it is appropriate to carry out the process in phenol or cresols. If, on the other hand, it is desired to synthesize polyisoindoxazenes, polycondensation should be performed in phenols with electron accepting substituents:



The course of the reaction is greatly influenced by the nature of the solvent in the case of the synthesis of polyquinoxalines from bis-β-diketones and tetramines [144]. The reaction rate in chloroform proved to be 10^5-10^6 times higher than in tetrahydrofuran.

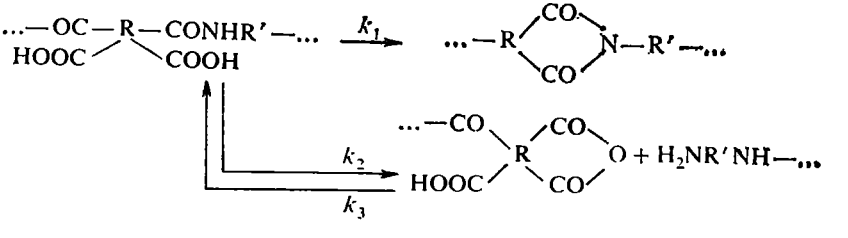
It can be seen from Table 2 that the reaction medium has a strong effect on the equilibrium constant and thereby on successful formation of polyimides. It was also found that the nature of the medium affects also the isomeric composition of polyamido acids in low tem-

perature acylation:



For instance, for the model reaction of tetracarboxydiphenyloxide with aniline in N-menthylpyrrolidone (N-MP) the isomeric composition is I : II : III = 0.46 : 0.11 : 0.43 whereas in dimethylsulphoxide (DMSO) it is 0.35 : 0.17 : 0.48. A similar relationship is observed for polyamido acids, the isomeric composition of the polymer being stable for prolonged intervals in N-MP and getting gradually enriched in structure I in DMSO [145].

In considering the polymer chain formation in the polyimide synthesis, the reversible character of the polyamido acid formation should be taken into account [126, 129, 146]. Particularly strongly the reversibility of the process manifests itself at elevated temperatures used in thermal cyclization of polyamido acids and leads to a sharp decrease in the molecular weight of the polymer at the initial cyclization stage. On the other hand, as the end groups accumulate, the reaction of polyimide synthesis acquires greater and greater importance. With all this in mind, one can depict cyclization by the following rough scheme:



showing that this process must be described not by one reaction rate constant but at least by three reaction rate constants.

In a two-stage method of polyoxadiazole formation, the second stage consists in the heterocycle closure. Thermal cyclization of polyhydrazides revealed an interesting feature: the cyclization activation energy grows in the course of the process as a result of an increase in the rigidity of the macromolecular chain [147].

In order to attain high levels of transformation of polyhydrazides into polyoxadiazole by thermal cyclization, very severe conditions

are usually required (prolonged thermal treatment at 300 °C in vacuum). Recently, on an example of cardo polymers it has been found that this procedure can be avoided by chemical cyclodehydration of polyhydrazides. The complexes of dimethylformamide (DMF) or dimethylacetamide (DMA) with sulphur trioxide are highly effective dehydrating agents for this purpose. Cyclization of polyhydrazide into polyoxadiazole in these complexes at 100 °C was accomplished with a quantitative yield in five hours [113].

The use of catalytic systems in the macromolecule formation by polycyclization proved to be promising also in other cases as well, e.g. in the synthesis of polyimides [63, 64, 148]. Because of the possibility of chemical cyclization (with alkaline acetates, mixtures of acetic anhydride with various tertiary amines, etc. used as catalysts) at rather low and even room temperatures, soluble polyimides with reactive groups (e.g. cardo polyimides of 3,3′,4,4′-benzophenone tetracarboxylic acid) can be successfully obtained.

The outcome of polycondensation, the chain growth, and the macromolecule formation largely depend on the reactivity of the initial substances, the understanding of its changes in the course of the reaction, and the skill in controlling it. The problem of the reactivity of different monomers in polycondensation processes has been discussed in many books and papers [8, 9, 14-17, 59, 60, 63-65, 92-98, 128, 134, 149-164].

Earlier we discussed the effect of salt formation on the reactivity of the amino groups in tetramines [59, 60]. It was shown also using an example of the reaction between *o*-phenylenediamine and *m*-carborane dicarboxylic acid chloride [159] that the influence of the structure of the tertiary amine (in whose presence the process is carried out) on the reactivity of amino groups is strong. For instance, in polycondensation in the presence of tributyl- or trioctylamines, the reactivity of the second amino group, after the first one has reacted, decreases by a factor of 30 or 50 while in the presence of triethylamine only by a factor of 2. This provides the possibility to control the polymer chain structure in polycondensation of aromatic tetramines with the carborane dicarboxylic acid chloride: either linear polyamido amines or polymers of branched and cross-linked structure can be obtained by use of tertiary amines of adequate structure in the process.

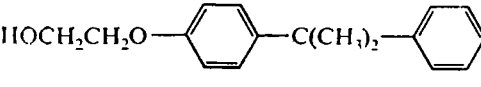
Studies of the reactivity of the amino groups in aromatic diamines in low-temperature polyamidation in dimethyl acetamide demonstrated that the first amino groups in *p*- and *m*-phenylenediamines are more active [134]. However, in the synthesis of poly-*m*-phenyleneisophthalamide only the first groups of the initial diamine react at a higher rate; the amino groups of all subsequent oligomers are equal in activity. The influence of the reactivity of acid halides in the synthesis of polyamides was also studied [160].

A relationship between the chemical structure of some tetracarboxylic acid dianhydrides and diamines in the acylation reactions was established. The reaction rate increases with the growth of the basicity of the amino groups and the electrophilic character of the anhydride groups [128]. It was found that the complexes of tetracarboxylic acid dianhydrides with polar solvents are less reactive in acylation of diamines than corresponding free anhydrides [161].

Systematic studies of the activity of many diols and dicarboxylic acid chlorides in acceptor-catalytic polyesterification were carried out [19, 22, 149-158]. It was convincingly shown that depending on the nature of the reactants, the activity of the second functional group of the monomer after the first one has reacted can decrease, remain unchanged or grow [155]. Some polymers (polyarylates [165, 166], polyhydrazide [167]) synthesized by non-equilibrium polycondensation feature a narrower molecular-weight distribution (polydispersity coefficient ≈ 1.5) than the most probable value. This suggests that the principle of the independent reactivities of the end groups is violated not only at the initial stages of interaction. An analytical solution of the kinetic equation describing time variation of the molecular-weight distribution of the non-equilibrium polycondensation products was made [162]; the authors also proposed a kinetic scheme of non-equilibrium polycondensation of monomers whose reaction centres can change their activity in the course of the process.

The effect of the reactivity of the functional groups on the regularities of formation of macromolecules of different microstructure is exceptionally important in non-equilibrium polycondensation. Investigations into acceptor-catalytic polyesterification made a large contribution to the solution of this problem. It was on an example of this process that the main regularities of the formation of macromolecules on the basis of diols with an unsymmetrical location of hydroxyl groups [168-171] and of macromolecules of mixed polymers obtained by non-equilibrium copolycondensation [19, 22, 163, 172-177] were formulated.

A possibility of the formation of the polymer chain in the "head-to-head" or "head-to-tail" arrangement arises in polycondensation of bifunctional compounds with an unsymmetrical location of functional groups (e.g. terephthaloyl chloride with



. It was found that in the case when at the beginning of acceptor-catalytic polyesterification both initial monomers are in solution, the polymer whose distribution of units is close to random is formed, irrespective of the difference in the activity levels of

the hydroxyl groups (for the β-hydroxyethyl ether of diphenylolpropane this difference is almost tenfold). The polymer with the predominance of the "head-to-head" or "tail-to-tail" combinations is formed only on gradual addition of the monomer with an unsymmetrical location of functional groups to the reaction zone [168-171].

The main regularities of the formation of macromolecules of mixed polymers in non-equilibrium polycondensation were examined on an example of acceptor-catalytic copolycondensation of a bisphenol and a glycol (comonomers) with terephthaloyl chloride (intermonomer) in a homogeneous system [19, 22, 163, 172-177]. It turned out that depending on the reactivities of the comonomers and the rate of introduction of the intermonomer into the reaction, both random and block copolymers can be produced. By varying these factors, one can obtain block copolymers with different block lengths, thus controlling the properties of the copolymers in the desired direction.

A number of mixed polymers were also prepared by such a kind of non-equilibrium polycondensation as interfacial polycondensation. These were various mixed polyamides, polyarylates, polyamidoarylates [9, 15]. In some cases the non-uniformity of the composition of such copolymers was noted which was caused by the formation of their macromolecules under the heterogeneous conditions of interfacial polycondensation and the attendant diffusion factors and also by different reactivities of comonomers in relation to the intermonomer [173, 174].

Interesting results were achieved in studying the formation of mixed polyimide macromolecules [115, 174]. In the one-stage synthesis of copolyimides with five- and six-membered cycles by polycyclization in solution, the copolyimide microstructure depends on the comonomer reactivities, the difference in the functional activity group of the intermonomer, the reaction procedure, and the stability of the imide cycles to destructive exchange reactions. When 3,3′,4,4′-tetracarboxydiphenyloxide dianhydride is used in the one-stage polycyclization, intense aminolysis results in the formation of random copolymers whereas in the presence of much more active pyromellitic dianhydrido the synthesis of copolyamides of block structure is possible. The microstructure of more aminolysis-resistant copolynaphthoyleneimides can be changed purposefully by varying the reaction conditions. Random copolyimides result from a simultaneous introduction of the initial substances and the catalyst into the reaction whereas the addition of the intermonomer together with the catalyst to the solution of the diamine mixture gives rise to block copolyimides. If copolyimides are synthesized in two stages when some type of distribution of units is predetermined at the polyamido acid formation stage, cyclization in mild conditions under the action of chemical agents makes the formation of block copolyimides pos-

sible. Alternatively, thermal cyclization leads to the formation only of random copolyimides.

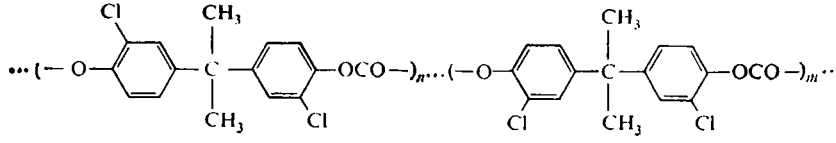
Wide possibilities of constructing the polymer chain are offered by polycondensation on the basis of reactive oligomers and polymers. Exchange interactions between mixtures of various polyesters, polyamides, polyesters with polyamides, heterochain polymers with monomers in equilibrium polycondensation were studied; it was shown that under certain process conditions the first stage involves the formation of block copolymers which further on, as the process goes on, transform into random copolymers by exchange reactions [8, 13, 33, 176-178]. However, the synthesis of block copolymers by equilibrium polycondensation is a rather difficult task because of exchange reactions.

Recent progress in obtaining polycondensation block copolymers from oligomers and polymers with functional end groups as initial substances is undoubtedly connected with advances in non-equilibrium polycondensation and first of all acceptor-catalytic polycondensation mild conditions which allow eliminating exchange transformations and therefore retaining the blocks of the initial polymers in the microstructure of the polymer chain unchanged. Practicable are at least three possible methods of synthesis of such block copolymers from oligomers: (1) polycondensation of oligomers differing in chemical structure with heterofunctional end groups; (2) polycondensation of oligomers differing in chemical structure having homofunctional groups with an intermonomer; (3) polycondensation of an oligomer and a low molecular monomer with an intermonomer [45, 179-184]. It is natural that depending on the preparation method and the chemical structure of the oligomer, the length of the structurally different blocks and their distribution along the macrochain will vary. Block copolymers of the most regular structure will be obtained by acceptor-catalytic polycondensation by the first method.

In considering the formation of macromolecules by polycondensation, it would be appropriate to discuss yet another problem. Until recent time, stereoregular polymers have been obtained by polycondensation only from initial compounds of quite definite configuration, i.e. from geometrical or optical isomers.

Profound investigations into non-equilibrium polycondensation created theoretical prerequisites for the synthesis of a new type of stereoregular polycondensation polymers whose macromolecules contain regular sequences of stable rotational isomers [19, 22, 185-188]. The fundamental novelty of the synthesis of conformationally regular polymers consists in the fact that the formation of their regular steric microstructure occurs directly during the macromolecule growth with the use of monomers which are not conformation or configuration isomers but whose molecules contain fragments with hindered internal rotation. Polymers of this kind are exemplified by

stereoregular polyterephthalates based on *o,o'*-disubstituted dian, e.g. *o,o'*-dichloro-*p,p'*-diphenylolpropane-2,2:



A comparison of the stereotacticity of the resulting polymers with synthesis conditions made it possible to formulate a number of regularities of the formation of such macromolecules. For instance, polymers with *cis* isomers of the bisphenol fragment are predominantly formed in the presence of weakly basic heterocyclic tertiary amines (nucleophilic catalysis) whereas those with *trans* isomers are formed in the presence of strongly alkaline trialkylamines (general basic catalysis) which is connected with the different geometry of the transition complexes. Undoubtedly, many problems concerning the mechanism of this process remain unclear and call for their solution. However, the available data suggest that stereoregular polycondensation polymers can be formed (i.e. polymer conformers) under certain conditions, which is a common feature inherent in all polymers whose macromolecules contain fragments with hindered internal rotation. Since the stereotacticity of such polymers is formed directly in the polycondensation process, it would be appropriate to call this process the conformation-specific polycondensation.

4.3. Termination of Chain Growth

The third stage through which every polymeric molecule passes in the polycondensation process is termination of chain growth under the action of both physical and chemical factors [8, 9, 19].

The chemical factors include: (1) limiting the macromolecule growth due to the process reversibility in the case of equilibrium polycondensation; (2) non-equivalent ratio of the initial substances; (3) the effect of reactive monofunctional impurities; (4) chemical changes in the functional groups of the macromolecules and of the monomers converting them to unreactive groups and the consequent disturbance of the equivalence of the ratio of the reactive groups.

The influence of the second and third factors has been extensively discussed in the literature [6-17]. Much attention is now being paid to the fourth factor as well.

In the previous sections discussing macromolecular chain initiation and growth during polycondensation we emphasized the strong influence of the reactivity of the monomers used. The third, last

stage of the formation of the macromolecule—chain termination—should also be drastically affected by the reactivity of the monomers and their chemical nature.

Acceptor-catalytic polyesterification is likely to be the first example of non-equilibrium polycondensation process for which the relationship between the molecular weight of the resulting polymers and the reactivity of the initial compounds has been established experimentally [136, 139, 189, 190]. It was found that the termination of the propagating macromolecules in acceptor-catalytic polyesterification is mainly due to acid halide groups participating in hydrolysis and aminolysis. An increase in the reactivity of diols under these conditions reduces the proportion of the chain termination reactions; as a result, the molecular weight of the polymer increases. An increase in the reactivity of acid halides can lead both to the increase and the decrease of the molecular weight of the polymer. When the increase in the reactivity of the monomer is accompanied by an increase in the contribution of the chain termination reactions, the molecular weight of the polymer goes down. The change from phenols to glycols and from strongly basic tertiary amines to weakly basic ones in acceptor-catalytic polyesterification increases the contribution of the side hydrolysis of acid halide groups, thus stimulating polymer chain termination at an earlier stage. Thus, the molecular weight of polymers in non-equilibrium polycondensation depends on the ratio between the rates of chain growth and chain termination.

Many non-equilibrium polycondensation processes are carried out in solution. The necessary condition for obtaining high molecular polymers is the chemical inertness of the solvent with respect to the resulting polymer and to the side processes involving the functional groups of the monomers and macromolecules and leading to their deactivation. Progress in non-equilibrium polycondensation resulted in broad application of aprotic solvents. Sometimes these are not only a good dissolving medium but also process activators and the acceptors of the low molecular polycondensation product. At the same time some authors have reported stimulation of undesirable side processes by these solvents giving rise to a premature chain termination [9]. Thus, low molecular weights of aromatic polyamides synthesized in dimethylformamide result from the side reaction between acid chloride and the solvent [191]. The process of acceptor-catalytic polyesterification does not run at all in dimethylacetamide and dimethylformamide [192]. Thus, when active solvents (dimethylacetamide, N-methylpyrrolidone, dimethylformamide, hexamethylformamide, etc.) are used in polycondensation, it is necessary to bear in mind and ideally to have knowledge of the full range of the effect that they can produce under real polycondensation conditions.

5. OTHER SIDE REACTIONS

Consideration of chemical formation of a polymer chain in polycondensation processes would be incomplete if no mention was made of a very important point, namely, that polycondensation processes, like other methods of synthesis of high molecular compounds, are often accompanied, apart from chain termination side reactions, by other side transformations resulting in the appearance of anomalous units in the macromolecules. As a result, the so-called "raznozvenny" (different-unit) polymers are formed, the concept that has been developed successively by Korshak [107, 193]. In fact all polymers synthesized by polycondensation, as by the way are all other polymers, are raznozvenny to a greater or lesser extent.

On the one hand, this different-unit structure can be created over a certain range consciously; on the other hand, it arises spontaneously. An example of consciously formed raznozvennost' (different-unit structure) can be provided by the synthesis of different mixed and block copolymers by non-equilibrium copolycondensation of several reactive bifunctional substances discussed above. The knowledge of the regularities of these processes enables their control and hence the control of raznozvennost' of the resulting polymeric chain. However, these processes include also spontaneous moments caused by the appearance of spontaneous raznozvennost' in the consciously created one. Both the kinetic factors caused by the difference in the functional group reactivity and various side processes can be responsible for them.

Mild conditions for a number of non-equilibrium polycondensation processes could seemingly exclude some undesirable side processes. However, it should be borne in mind that such conditions are ensured by high reactivity of initial substances, specificity of the media or catalysts; all these factors may sometimes easily stimulate side processes as well.

Causes of the appearance of raznozvenny polymers, formation of anomalous units in the ircomposition in polycondensation are diverse. These are isomerization of some fragments, different combinations of unsymmetrical units or steric conformers, branching of macromolecules, and many other side processes caused by the specific chemical structure of some macromolecule fragments. The understanding of these processes and raznozvenny polymers caused by them, their conversion from spontaneous to consciously directed and controlled is of great importance at the present stage of polymer science development since it is closely connected with the problem of a purposeful synthesis of polymers with a desired set of properties.

At present, a vast body of experimental data pertaining to concrete dependences (the effect of temperature and time of reaction, the ratio of the initial substances, the nature of the solvent, the order and

the rate of introduction of the reactants into the system, and the concentration of the reactants on the molecular weight, polydispersity, and yield of polymers) is available in the literature concerning various polycondensation processes [5-15, 194, 195].

6. NEW POLYMERS AND REACTIONS

The domain of polycondensation continues its intense development both in the field of the understanding of the regularities of the polycondensation processes and in the sphere of the utilization of this method in the synthesis of various new polymers.

Thus, polycyclization afforded different polymers of cyclolinear and ladder structure with improved thermal characteristics [9, 13, 21, 25, 62-66, 196-208]. A new method, i.e. reduction polyheterocyclization, has recently been proposed for the synthesis of cyclochain polymers; this method opens up possibilities of obtaining the polymers from more accessible raw materials, such as nitro derivatives [197].

The development of polycyclocondensation processes resulted in the synthesis of a number of new polymers of the polyphenylene type [79-88]. Polycondensation of tetranitriles of tetracarboxylic acids with diamines gave nitrogen-containing polymers with macroheterocycles in their chain and polyisoindoxazenes [39, 40]; polycondensation with triaminobenzenes and bis(*o*-cyanamines) of aromatic compounds afforded macroheterocyclic polymers containing condensed isoindole and benzimidazole and also isoindole and quinazoline cycles [209]. Polycondensation of tetranitriles of tetracarboxylic acids with bisanthranilic acids resulted in the synthesis of new polymers containing condensed isoindole and quinazoline cycles [210].

Various polycondensation processes formed the basis for the development of chemistry of cardo polyheteroarylenes whose distinctive feature is the presence of a carbon atom in the repeating unit which is included in the cyclic side group. These polymers possess valuable properties and combine elevated heat stability and good solubility in organic solvents [211-213].

Polycondensation of polychlorodiphenylenes with sodium sulphide resulting in the formation of sulphur- and chlorine-containing polymers [214] and polycondensation of dihalogenaromatic compounds with alkali metal sulphides [215, 216] were studied. New high molecular polyketones were synthesized by polycondensation of aromatic hydrocarbons, such as diphenyleneoxide and diphenyl, with dicarboxylic acids in polyphosphoric acid [217].

Tautomeric transformations of dibenzoylterephthalic and isophthalic acid chlorides were disclosed and investigated; on this basis their polycondensation with bisphenols giving polymers of two types — aromatic polyethers and aromatic polyesters—was carried out; the

methods of purposeful synthesis of high molecular aromatic polyethers containing phenoxyphthalide fragments were found [67].

Conformation-specific polycondensation was elaborated; this made it possible to synthesize new conformation-regular polyarylates. The presence of regular sequences of isomeric forms in the macromolecules of these polymers substantially influences their properties [19, 22, 185-189]. A series of polycondensation studies with the use of "activated" dicarboxylic esters (e.g. of the type of bispentachlorophenyl, bis-2,4-dinitrophenyl esters) offering possibilities of preparing heterochain polymers under mild conditions has been started [218-220].

Polycondensation has opened up wide possibilities for the synthesis of various multiblock copolymers, e.g. polyarylatedimethylsiloxane, polyarylatearylenesulphoneoxide, polyarylateethyleneoxide, polyarylatebutadiene, etc., with a finely controlled microstructure and a wide range of properties—from thermoplastics to elastoplastics [45, 179, 180, 184].

Oxidative dehydropolycondensation was used for the synthesis of a linear polymer of carbon, "carbine", which is a new allotropic form of carbon [221]. Polycondensation resulted in the formation of many coordination polymers both with organoelement and inorganic main macromolecular chains [222-224]. Diverse polycondensation processes made the basis for chemistry of carborane-containing polymers of different classes. A distinctive feature of such polymers, particularly of polyheteroarylenecarboranes, is high thermal stability of materials on their basis [225-227, 229].

Polycondensation processes are widely presented in chemistry of organosilicon and organosiliconelement polymers [18, 228].

It stands to reason that the limited volume of the present review does not allow mentioning all new achievements in polycondensation over the past 50 years. However, even the examples discussed here show clearly high efficiency and promising future of this important method of polymer formation as well as the necessity of its further development both in the direction of a deeper understanding of the process mechanisms, the finding of the relationships between the kinetic parameters and the mechanism of the elementary chemical acts, in purposeful catalysis, the control of the regularities of the microstructure formation, the molecular weight and the molecular-weight distribution of polymers, the control of the anomalous unit formation giving rise to different-unit polymers, the optimization of the production processes and also in the direction of producing new polymers by polycondensation with high thermal stability, elasticity, strength, hardness, incombustibility, a valuable set of electrical, medical, biological and other properties, etc., the polymers which will be able to meet growing requirements placed by modern engineering and economics.

References

1. J. Gay-Lussak and J. Pelouse, *Ann.*, 7, 40 (1833).
2. A.M. Butlerov, *Ann.*, 35, 242 (1859).
3. N.N. Menshutkin, *Ber.*, 13, 523 (1881).
4. G.S. Petrov, B.N. Rutovsky, and I.P. Losev, *Technology of Synthetic Resins and Plastics*, Goskhimizdat, Moscow-Leningrad, 1946, p. 52 (in Russian).
5. V.V. Korshak and S.R. Rafikov, *Synthesis and Studies of High-molecular Compounds*, Izd. Acad. Nauk SSSR, Moscow-Leningrad, 1949 (in Russian).
6. V.V. Korshak, *Chemistry of High-molecular Compounds*, Izd. Akad. Nauk SSSR, Moscow-Leningrad, 1950 (in Russian).
7. V.V. Korshak, *Methods of High-molecular Organic Chemistry*, Izd. Akad. Nauk SSSR, Moscow, 1953 (in Russian).
8. V.V. Korshak and V.S. Vinogradova, *Equilibrium Polycondensation*, Nauka, Moscow, 1968 (in Russian).
9. V.V. Korshak and S.V. Vinogradova, *Non-equilibrium Polycondensation*, Nauka, Moscow, 1972 (in Russian).
10. V.V. Korshak and S.V. Vinogradova, *Heterochain Polyesters*, Izd. Akad. Nauk SSSR, Moscow, 1958 (in Russian).
11. V.V. Korshak and T.M. Frunze, *Synthetic Heterochain Polyamides*, Izd. Akad. Nauk SSSR, Moscow, 1962 (in Russian).
12. V.V. Korshak and S.V. Vinogradova, *Polyesters*, Pergamon Press, London-New York-Paris, 1965.
13. V.V. Korshak, *Progress in Polymer Chemistry*, Nauka, Moscow, 1965 (in Russian).
14. L.B. Sokolov, *Polycondensation Method of Polymer Synthesis*, Khimiya, Moscow, 1966 (in Russian).
15. L.B. Sokolov, *Fundamentals of Polymer Synthesis by Polycondensation*, Khimiya, Moscow, 1979 (in Russian).
16. B.A. Zhubanov, *Introduction to the Chemistry of Polycondensation Processes*, Nauka, Kaz. SSR, Alma-Ata, 1974 (in Russian).
17. *Polycondensation Processes and Polymers, Collected Papers*, Kabardino-Balkarsk University Press, Nal'chik, 1979 (in Russian).
18. K.A. Andrianov, *Polymers with Inorganic Main Molecular Chains*, Izd. Akad. Nauk SSSR, Moscow, 1962 (in Russian).
19. S.V. Vinogradova, *Vysokomolek. Soed.*, A19, 667 (1977).
20. V.V. Korshak, *Vysokomolek. Soed.*, A21, 3 (1979).
21. S.V. Vinogradova and V.V. Korshak, *Usp. Khimii*, 39, 679 (1970).
22. V.A. Vasnev and S.V. Vinogradova, *Usp. Khimii*, 48, 30 (1979).
23. V.V. Korshak, *Acta Polymerica*, 31, 90 (1980); 34, 603 (1983).
24. V.V. Korshak, *Usp. Khimii*, 51, 2096 (1982).
25. V.V. Korshak, *Usp. Khimii*, 53, 3 (1984).
26. S.V. Vinogradova, in: *Progress in Polymer Chemistry*, Nauka, Moscow, 1969, p. 113 (in Russian).
27. V.V. Korshak and K.K. Mozgova, *Usp. Khimii*, 28, 783 (1959).
28. V.V. Korshak, in: *Polycondensation Processes, Collected Papers*, Izd. BAN, Sofia, 1976.
29. V.V. Korshak, ed., *Technology of Plastics*, Moscow, Khimiya, 1985 (in Russian).
30. V.V. Korshak, *Itogi Nauki i Tekhniki, Chemistry and Technology of High-molecular Compounds*, Vol. 7, VINITI, 1975, p. 5 (in Russian).
31. V.V. Korshak, *Acta Chim. Acad. Sci. Hung.*, 81, 345 (1974).
32. V.V. Korshak, in: *Kinetics and Mechanism of Formation and Transformation of Macromolecules, Collected Papers*, Nauka, Moscow, 1968, p. 127 (in Russian).
33. V.V. Korshak, *Pure Appl. Chem.*, 12, 101 (1966).

34. A.N. Pravednikov, I.E. Kardash, I.P. Glukhoedov, and A.Ya. Ardashnikov, *Vysokomolek. Soed.*, A15, 349 (1973).
35. A.Ya. Ardashnikov, I.E. Kardash, and A.N. Pravednikov, *Vysokomolek. Soed.*, A13, 1863 (1971).
36. B.A. Zhubanov, in: *Polycondensation Processes and Polymers, Collected Papers*, Kabardino-Balkarsk University Press, Nal'chik, 1979, p. 139 (in Russian).
37. E.V. Kamzolkina, G.A. Teyes, P.P. Nechaev, Z.V. Gerashchenko, and Ya.S. Vygodsky, *Vysokomolek. Soed.*, A18, 2764 (1976).
38. S.V. Vinogradova, Ya.S. Vygodsky, T.I. Spirina, L.I. Chudina, and V.V. Korshak, *Vysokomolek. Soed.*, A21, 1064 (1979).
39. S.V. Winogradova, S.A. Siling, and W. Solowjöw, *Makromol. Chem.*, 177, 1905 (1976).
40. S.V. Vinogradova, V.V. Korshak, S.A. Siling, and W.N. Solovjov, *J. Polymer Sci.*, 22, 1043 (1984).
41. I.B. Rabinovich, N.V. Karyakin, E.S. Dzharimova, S.A. Siling, I.I. Ponomarev, and S.V. Vinogradova, *Izv. Akad. Nauk SSSR, OKhN*, 779 (1984).
42. S.V. Vinogradova, S.A. Siling, V.N. Solov'yev, and V.V. Korshak, *Zh. Org. Khim.*, 10, 2437 (1974).
43. S.A. Siling, I.I. Ponomarev, V.V. Kuznetsov, S.V. Vinogradova, and V.V. Korshak, *Izv. Akad. Nauk SSSR, OKhN*, 771 (1984).
44. S.A. Siling, I.I. Ponomarev, V.V. Kuznetsov, B.V. Lokshin, V.S. Vinogradova, and V.V. Korshak, *Izv. Akad. Nauk SSSR, OKhN*, 1755 (1983).
45. S.V. Vinogradova, in: *Polycondensation Processes and Polymers, Collected Papers*, Kabardino-Balkarsk University Press, Nal'chik, 1979, p. 95 (in Russian).
46. V.V. Korshak, *Vysokomolek. Soed.*, A24, 1571 (1982); *Dokl. Akad. Nauk SSSR*, 268, 910 (1983).
47. V.V. Korshak and Yu.V. Korshak, *Vysokomolek. Soed.*, A26, 16 (1984).
48. V.V. Korshak and Yu.V. Korshak, *Dokl. Akad. Nauk SSSR*, 275, 400 (1984).
49. V.V. Korshak, S.L. Sosin, and M.V. Chistyakova, *Izv. Akad. Nauk SSSR, OKhN*, 1271 (1957).
50. V.V. Korshak and S.L. Sosin, *Priroda*, No. 4, 98 (1962).
51. V.V. Korshak, IUPAC, *Macromolecules*, Pergamon Press, Oxford-New York, 1982, p. 1.
52. V.V. Korshak, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, No. 5, 2 (1981).
53. R.H. Kienle, *Ind. Eng. Chem.* 22, 590 (1930).
54. W.H. Carothers, *Trans. Faraday Soc.*, 32, 39 (1936).
55. V.I. Irzhak, B.A. Rozenberg, and N.S. Enikolopov, *Network Polymers*, Nauka, Moscow, 1979, p. 42 (in Russian).
56. S.G. Entelis, V.V. Evreinov, and A.N. Kuzaev, *Advances in Polymer Chemistry and Physics*, Khimiya, Moscow, 1973, p. 201 (in Russian).
57. V.V. Korshak, *Dokl. Akad. Nauk SSSR*, 262, 1149 (1982).
58. V.V. Korshak, T.M. Frunze, V.V. Kurashev, and G.V. Kotrelev, *Vysokomolek. Soed.*, 5, 979 (1963).
59. V.V. Korshak, N.I. Bekasova, and V.V. Vagin, *Vysokomolek. Soed.*, B15, 6 (1973).
60. V.V. Korshak, N.I. Bekasova, V.V. Vagin, and A.A. Izyneev, *Dokl. Akad. Nauk SSSR*, 210, 110 (1973).
61. V.V. Korshak, N.I. Bekasova, M.A. Surikova, L.I. Komarova, and I.Yu. Voloshina, *Vysokomolek. Soed.*, A23, 138 (1981).
62. V.V. Korshak, *Thermostable Polymers*, Nauka, Moscow, 1969 (in Russian).
63. M.I. Bessonov, M.M. Koton, V.V. Kudryavtsev, and L.A. Layus, *Polyimides, a Class of Thermostable Polymers*, Nauka, Leningrad, 1983 (in Russian).
64. N.A. Adrova, M.I. Bessonov, L.A. Layus, and A.P. Rudakov, *Polyimides*,

a New Class of Thermostable Polymers, Nauka, Leningrad, 1968 (in Russian).
65. B.A. Zhubanov, I.A. Arkhipova, and O.A. Almabekov, *New Thermostable Heterocyclic Polymers*, Nauka, Alma-Ata, 1979 (in Russian).
66. K.A. Andrianov, M.M. Ilyin, V.N. Talanov, L.S. Isakova, and N.A. Sidorenko, *Vysokomolek. Soed.*, A18, 2752 (1976).
67. S.N. Salazkin, V.V. Korshak, S.V. Vinogradova, G.N. Melekhina, A.A. Kul'kov, and L.I. Komarova, *Vysokomolek. Soed.*, A19, 181 (1977).
68. S.V. Vinogradova, S.N. Salazkin, G.N. Melekhina, L.I. Komarova, and V.V. Korshak, *Vysokomolek. Soed.*, A22, 2768 (1980).
69. V.V. Korshak, S.V. Vinogradova, and S.A. Siling, *Vysokomolek. Soed.*, 8, 1608 (1966).
70. V.V. Korshak, S.V. Vinogradova, S.A. Siling, S.R. Rafikov, Z.Ya. Fomina, and V.V. Rode, *J. Polymer. Sci.*, A-1,7, 157 (1969).
71. V.V. Korshak, S.V. Vinogradova, M.G. Vinogradov, and Yu.A. Davidovich, *Vysokomolek. Soed.*, 6, 2149 (1964).
72. V.V. Korshak, S.V. Vinogradova, and M.G. Vinogradov, *Vysokomolek. Soed.*, 6, 1987 (1964).
73. S.V. Vinogradova, V.V. Korshak, and M.G. Vinogradov, *J. Polymer Sci.*, C, 2565 (1967)
74. V.V. Korshak, in: *Polycondensation Processes and Polymers, Collected Papers*, Kabardino-Balkarsk University Press, Nal'chik, 1979, p. 45 (in Russian).
75. V.V. Korshak, *Faserforsch. u. Textiltechnik*, 28, 561 (1977).
76. S.V. Vinogradova, Ya.S. Vygodsky, N.A. Churochkina, and V.V. Korshak, *Vysokomolek. Soed.* B19, 93 (1977).
77. S.V. Vinogradova and J.S. Vygodskij, *Faserforsch. u. Textiltechnik*, 28, 581 (1977).
78. V.V. Korshak, S.V. Vinogradova, and J.S. Vygodskij, *Faserforsch. u. Textiltechnik*, 28, 439 (1977).
79. V.V. Korshak, M.M. Teplyakov, and V.A. Sergeev, *Vysokomolek. Soed.*, B14, 800 (1972); *Dokl. Akad. Nauk SSSR*, 208, 1360 (1973).
80. V.V. Korshak, M.M. Teplyakov, V.P. Chebotarev, V.A. Li, and V.M.Kalinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1091 (1973).
81. M.M. Teplyakov and V.P. Chebotarev, *Acta Chim. Acad. Sci. Hung.*, 81 (2-3), 281 (1974).
82. B.V. Rozynov, M.M. Teplyakov, V.P. Chebotarev, and V.V. Korshak, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1602 (1974).
83. V.V. Korshak, M.M. Teplyakov, D.M. Kakuridze, and N.V. Kravchenko, *Dokl. Akad. Nauk SSSR*, 219, 117 (1974).
84. V.V. Korshak and M.M. Teplyakov, *Vysokomolek. Soed.*, A16, 497 (1974).
85. M.V. Shishkina, M.M. Teplyakov, V.P. Chebotarev, and V.V. Korshak, *Vysokomolek. Soed.*, A17, 1510 (1975).
86. V.V. Korshak, M.M. Teplyakov, I.A. Khotina, and V.P. Chebotarev, *Vysokomolek. Soed.*, B17, 504 (1975).
87. V.V. Korshak, M.M. Teplyakov, and R.A. Dvorikova, *Vysokomolek. Soed.*, A24, 277 (1982).
88. V.V. Korshak and S.V. Vinogradova, *Polyarylates*, Nauka, Moscow, 1964 (in Russian).
89. S.V. Vinogradova, in: *Progress in Polymer Chemistry*, Nauka, Moscow, 1969, p. 113 (in Russian).
90. S.V. Vinogradova, *J. prakt. Chemie*, 313, 397 (1971).
91. R.S. Velichkova, V.V. Korshak, S.V. Vinogradova, N.V. Ivanov, A.I. Ponomarenko, and N.S. Enikolopov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 858 (1969).
92. S.V. Vinogradova, V.V. Korshak, V.A. Pankratov, and D.R. Tur, *Dokl. Akad. Nauk SSSR*, 164, 563 (1965).
93. S.V. Vinogradova and V.V. Korshak, *Dokl. Akad. Nauk SSSR*, 123, 849 (1959).

94. V.V. Korshak, S.V. Vinogradova, P.M. Valetsky, and A.N. Baskakov, *Dokl. Akad. Nauk SSSR*, 174, 849 (1967).
95. S.V. Vinogradova, V.V. Korshak, G.Sh. Papava, N.A. Maisuradze, and R.S. Velichkova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 820 (1970).
96. S.V. Vinogradova, V.V. Korshak, Yu.V. Mironov, and P.M. Valetsky, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 245 (1966).
97. V.V. Korshak, I.A. Gribova, and M.A. Andreeva, *Vysokomolek. Soed.*, 2, 427 (1960).
98. D. Israilov, L.A. Rodivilova, and M.S. Akutin, *Plast. Massy*, No. 9, 13 (1966).
99. M.I. Siling, *Phenol-formaldehyde Polymers, Itogi Nauki i Tekhniki, Chemistry and Technology of High-molecular Compounds*, Vol. 11, VINITI, Moscow, 1977, p. 35 (in Russian).
100. V.V. Korshak, S.V. Vinogradova, and V.A. Vasnev, *Dokl. Akad. Nauk SSSR*, 191, 614 (1970).
101. S.V. Vinogradova, V.A. Vasnev, V.V. Korshak, A.V. Vasil'yev, and Yu.I. Perfilov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2138 (1970).
102. V.A. Vasnev, S.V. Vinogradova, A.I. Tarasov, and V.V. Korshak, *Zh. VKhO im. D.I. Mendeleeva*, 17, 472 (1972).
103. V.V. Korshak, S.V. Vinogradova, A.I. Tarasov, V.A. Vasnev, and L.V. Morgunova, *Trudy MKhTI im. D.I. Mendeleeva*, No. 70, 84 (1972).
104. V.V. Korshak, V.A.Vasnev, S.V. Bogatkov, A.I. Tarasov, and S.V. Vinogradova, *Reakts. Sposob. Organich. Soed.*, 10, 375 (1973).
105. V.A. Vasnev, A.I. Tarasov, S.V. Vinogradova, and V.V. Korshak, *Vysokomolek. Soed.*, A17, 721 (1975).
106. S.L. Sosin, V.V. Korshak, and D.G. Val'kovsky, *Dokl. Akad. Nauk SSSR*, 155, 376 (1964).
107. V.V. Korshak, *Raznozvennost' of Polymers*, Nauka, Moscow, 1977 (in Russian).
108. V.V. Korshak and S.V. Vinogradova, *Dokl. Akad. Nauk SSSR*, 77, 277 (1951); *ZhOKh*, 22, 1176 (1952).
109. V.V. Korshak and S.V. Vinogradova, *Izv. Akad. Nauk SSSR, OKhN*, 537 (1953).
110. S.V. Vinogradova and V.V. Korshak, *Dokl. Akad. Nauk SSSR*, 123, 849 (1958).
111. S.V. Vinogradova, V.V. Korshak, R.S. Velichkova, and L.L. Reshetnikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1494 (1968).
112. V.V. Korshak, S.V. Vinogradova, P.M. Valetsky, and S.N. Salazkin, *Vysokomolek. Soed.*, 3, 72 (1961).
113. S.V. Vinogradova and D.R. Tur, *Vysokomolek. Soed.*, A15, 284 (1973).
114. S.V. Vinogradova, V.V. Korshak, Ya.S. Vygodsky, and B.V. Lokshin, *Vysokomolek. Soed.*, A9, 1091 (1967).
115. V.V. Korshak, S.V. Vinogradova, Ja.S. Vygodskii, Z.M. Nagiev, Ja.G. Urman, S.G. Alekseeva, and I.Ja. Slonim, *Macromol. Chem.*, 184, 235 (1983).
116. V.V. Korshak and S.V. Vinogradova, *Vysokomolek. Soed.*, A13, 367 (1971),
117. V.V. Korshak, V.A. Vasnev, and S.V. Vinogradova, *Vysokomolek. Soed.*, B9, 522 (1967).
118. S.V. Vinogradova, V.V. Korshak, Ya.S. Vygodsky, and V.I. Zaitsev, *Vysokomolek. Soed.*, A9, 653 (1967).
119. V.M. Savinov, L.B. Sokolov, A.V. Ivanov, S.S. Petis, E.P. Krasnov, G.A. Kuznetsov, and A.G. Ushakova, *Plast. Massy*, No. 6, 25 (1967).
120. L.B. Sokolov, V.D. Gerasimov, V.M. Savinov, and V.K. Belyakov, *Thermostable Aromatic Polyamides*, Khimiya, Moscow, 1975 (in Russian).
121. V.V. Korshak, G.L. Berestneva, and I.P. Bragina, *Vysokomolek. Soed.*, A14, 1036 (1972).
122. V.V. Korshak, G.L. Berestneva, I.P. Bragina, and I.V. Zhuravleva, *Dokl. Akad. Nauk SSSR*, 211, 598 (1973).

123. V.V. Korshak, G.L. Berestneva, I.P. Bragina, and G.V. Eremina, *Vysokomolek. Soed.*, **A16**, 1714 (1974).
124. V.V. Korshak, G.L. Berestneva, I.P. Bragina, and S.A. Astafyev, *J. Polymer Sci., Polymer Symp.*, **47**, 25 (1974).
125. N.V. Karyakin, A.N. Mochalov, I.B. Rabinovich, G.P.Kamelova, G.L. Berestneva, and S.A. Astaf'yev, *Vysokomolek. Soed.*, **A17**, 1888 (1975).
126. S.V. Vinogradova, Z.V. Gerashchenko, Ya.S. Vygodsky, F.B. Sherman, and V.V. Korshak, *Dokl. Akad. Nauk SSSR*, **203**, 821 (1972).
127. L.A. Layus, M.I. Bessonov, and D.S. Florinsky, *Vysokomolek. Soed.*, **A13**, 2006 (1971).
128. M.M. Koton, V.V. Kudryavtseva, N.A. Adrova, K.K. Kalnin'sh, A.M. Dubova, and V.M. Svetlichnyi, *Vysokomolek. Soed.*, **A16**, 2081 (1974).
129. P.P. Nechaev, Ya.S. Vygodsky, G.E. Zaikov, and S.V. Vinogradova, *Vysokomolek. Soed.*, **A18**, 1667 (1976).
130. Z.V. Gerashchenko, Ya.S. Vygodsky, G.L. Slonimsky, A.A. Askadsky, V.S. Papkov, *et al.*, *Vysokomolek. Soed.*, **A15**, 1718 (1973).
131. I.B. Rabinovich, A.P. Mochalov, L.I. Pavlinov, V.V. Korshak, A.L. Rusanov, and R.D. Katsarava, *Dokl. Akad. Nauk SSSR*, **198**, 597 (1971).
132. P.V. Karyakin, I.B. Rabinovich, V.V. Korshak, A.L. Rusanov, D.S. Tugushi, A.N. Mochalov, and V.N. Sapozhnikov, *Vysokomolek. Soed.*, **A16**, 691 (1974).
133. P.P. Nechaev, Yu.V. Moiseev, S.V. Vinogradova, Ya.S. Vygodsky, G.E. Zaikov, and V.V. Korshak, *Vysokomolek. Soed.*, **A15**, 702 (1973).
134. D.F. Sokolova and L.B. Sokolov, *Vysokomolek. Soed.*, **A16**, 1369 (1974).
135. V.V. Korshak, V.A. Vasnev, S.V. Vinogradova, and A.V. Vasil'yev, *Vysokomolek. Soed.*, **A16**, 502 (1974).
136. S.V. Vinogradova, V.A. Vasnev, V.V. Korshak, T.I. Mitaishvili, and A.V. Vasil'yev, *Dokl. Akad. Nauk SSSR*, **187**, 1297 (1969).
137. S.V. Vinogradova, V.A. Vasnev, V.V. Korshak, A.V. Vasil'yev, and L.V. Dubrovina, *Vysokomolek. Soed.*, **A13**, 770 (1971).
138. V.V. Korshak, S.V. Vinogradova, V.A. Vasnev, and A.V. Vasil'yev, *Vysokomolek. Soed.*, **A14**, 56 (1972).
139. V.V. Korshak, E.A. Turska, A.V. Vasil'yev, M. Sinyarska-Kapustinskaya, S.V. Vinogradova, and V.A. Vasnev, *Vysokomolek. Soed.*, **A14**, 1267 (1972).
140. S.V. Vinogradova, V.V. Korshak, A.V. Vasil'yev, and V.A. Vasnev, *Vysokomolek. Soed.*, **A15**, 2015 (1973).
141. V.V. Korshak, E.A. Turska, M. Sinyarska-Kapustinskaya, V.A. Vasnev, S.V. Vinogradova, S.A. Pavlova, A.V. Vasil'yev, and L.V. Dubrovina, *Vysokomolek. Soed.*, **B16**, 147 (1974).
142. V.V. Korshak, S.V. Vinogradova, and V.A. Vasnev, *Vysokomolek. Soed.*, **A10**, 1329 (1968).
143. V.V. Korshak, S.V. Vinogradova, V.A. Vasnev, and T.I. Mitaishvili, *Vysokomolek. Soed.*, **A11**, 81 (1969).
144. A.I. Kuzaev, V.V. Korshak, E.S. Krongauz, G.A. Mirontseva, and A.P. Travnikova, *Vysokomolek. Soed.*, **A25**, 396 (1983).
145. S.G. Alekseeva, S.V. Vinogradova, V.D. Vorob'yev, Ya.S. Vygodsky, V.V. Korshak, I.Ya. Slonim, T.N. Spirina, Ya.G. Urman, and L.I. Chudina, *Vysokomolek. Soed.*, **A21**, 2207 (1979).
146. E.V. Kamzolkina, P.P. Nechaev, V.S. Markin, Ya.S. Vygodsky, T.V. Grigor'yeva, and G.E. Zaikov, *Dokl. Akad. Nauk SSSR*, **219**, 650 (1974).
147. I.P. Bragina, V.V. Korshak, G.L. Berestneva, S.V. Vinogradova, D.R. Tur, V.A. Khomutov, and V.V. Krylova, *Vysokomolek. Soed.*, **A18**, 2318 (1976).
148. S.V. Vinogradova, Ya.S. Vygodsky, V.D. Vorob'yev, N.A. Churochkina, L.I. Chudina, T.N. Spirina, and V.V. Korshak, *Vysokomolek. Soed.*, **A16**, 506 (1974).

149. V.V. Korshak, S.V. Vinogradova, Yu.I. Perfilov, V.A. Vasnev, and A.I. Tarasov, *Trudy MKhTI im. D.I. Mendeleeva*, No. 70, 150 (1970).
150. S.V. Vinogradova, V.A. Vasnev, Yu.I. Perfilov, and V.V. Korshak, *Vysokomolek. Soed.*, **B14**, 457 (1972).
151. V.V. Korshak, A.P. Kreshkov, S.V. Vinogradova, N.Sh. Aldarova, V.A. Vasnev, E.L. Baranov, M.V. Slavgorskaya, A.I. Tarasov, and T.I. Mitaishvili, *Vysokomolek. Soed.*, **A11**, 73 (1969).
152. D.A. Bochvar, I.V. Stakevich, S.V. Vinogradova, V.V. Korshak, and V.A. Vasnev, *Dokl. Akad. Nauk SSSR*, **194**, 119 (1970).
153. S.V. Vinogradova, V.A. Vasnev, and V.V. Korshak, *Vysokomolek. Soed.*, **B15**, 600 (1971).
154. E.V. Bryukhova, V.V. Korshak, V.A. Vasnev, and S.V. Vinogradova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 599 (1972).
155. V.V. Korshak, S.V. Vinogradova, V.A. Vasnev, and A.I. Tarasov, *Vysokomolek. Soed.*, **A17**, 1212 (1975).
156. S.I. Kuchanov, M.L. Keshtov, P.G. Halatur, V.A. Vasnev, S.V. Vinogradova, and V.V. Korshak, *Macromol. Chem.*, **184**, 105 (1983).
157. V.A. Vasnev, M.G. Keshelava, V.V. Korshak, S.V. Vinogradova, N.G. Bekauri, and Ts.A. Goguadze, *Izv. Akad. Nauk SSSR*, **1**, 340 (1975).
158. A.K. Mikitaev, V.A. Vasnev, Yu.I. Musaev, E.B. Musaeva, and S.V. Vinogradova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2133 (1976).
159. V.V. Korshak, V.V. Vagin, N.I. Bekasova, and A.A. Izyneev, *Dokl. Akad. Nauk SSSR*, **212**, 118 (1973).
160. L.B. Sokolov, *Vysokomolek. Soed.*, **A15**, 387 (1973).
161. G.I. Boiko and B.A. Zhubanov, *Vysokomolek. Soed.*, **A16**, 554 (1973).
162. S.I. Kuchanov and L.I. Pis'men, *Vysokomolek. Soed.*, **A14**, 131, 886 (1972).
163. V.A. Vasnev and S.I. Kuchanov, *Usp. Khimii*, **52**, 2194 (1973).
164. S.I. Kuchanov, *Vysokomolek. Soed.*, **A15**, 2140 (1973); **A16**, 1125 (1974).
165. S.A. Pavlova, L.V. Dubrovina, and T.M. Orlova, *Vysokomolek. Soed.*, **A16**, 1673 (1974).
166. V.V. Korshak, S.A. Pavlova, L.V. Dubrovina, T.M. Orlova, V.A. Vasnev, A.V. Vasil'yev, and S.V. Vinogradova, *Vysokomolek. Soed.*, **A14**, 724 (1972).
167. V.V. Korshak, L.A. Pankratova, G.I. Timofeeva, S.A. Pavlova, D.R. Tur, and S.V. Vinogradova, *Paper Deposited at VINITI*, No. 5876-73, 1973; *RZhKhim*, 1973, 210198.
168. V.V. Korshak, S.V. Vinogradova, S.I. Kuchanov, V.A. Vasnev, G.D. Markova, and A.I. Tarasov, *Vysokomolek. Soed.*, **A16**, 1992 (1974).
169. V.V. Koršak, S.V. Vinogradova, V.A. Vasnev, D.G. Markova, and T.V. Lekae, *J. Polymer Sci., Polymer Chem. Ed.*, **13**, 2741 (1975).
170. Z. Jedlinski, D.Sek, U.Gaic, G.D. Marcova, V.A. Vasnjov, S.V. Vinogradova, and V.V. Korshak, *Acta Polym.*, **31**, 100 (1980).
171. I.Ya. Slonim, V.A. Vasnev, A.Kh. Bulai, Ya.G. Urman, G.D. Markova, V.V. Korshak, and S.V. Vinogradova, *Vysokomolek. Soed.*, **A22**, 2792 (1980).
172. V.V. Korshak, S.V. Vinogradova, P.O. Okulevich, Yu.I. Perfilov, V.A. Vasnev, and E.I. Fedin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1629 (1972).
173. V.V. Korshak, S.V. Vinogradova, T.M. Frunze, L.V. Kozlov, and Ban-Yuan U, *Vysokomolek. Soed.*, **4**, 1457 (1963).
174. V.V. Korshak, S.V. Vinogradova, and Ban-Yuan U, *Vysokomolek. Soed.* **5**, 969, 1765 (1963).
175. Ya.S. Vygodsky, S.V. Vinogradova, Z.M. Nagiev, V.V. Korshak, Ya.G. Urman, G. Rainish, and G. Rafler, *Acta Polym.*, **33**, 131 (1982).
176. V.V. Korshak, T.M. Frunze, I-Nan Lu, *Vysokomolek. Soed.*, **2**, 984 (1960); **3**, 665 (1961).
177. V.V. Korshak, S.V. Vinogradova, M.M. Teplyakov, and Yu.A. Chernomordik, *Dokl. Akad. Nauk SSSR*, **147**, 1365 (1962).

178. V.V. Korshak, S.V. Vinogradova, M.M. Teplyakov, R.D. Fedorova, and G.Sh. Papava, *Vysokomolek. Soed.*, 8, 2155 (1966).
179. P.M. Valetsky and I.P. Storozhuk, *Usp. Khimii*, 48, 75 (1979).
180. S.B. Dolgoplosk, V.P. Mileshkevich, P.M. Valetsky, *et al.*, *Vysokomolek. Soed.*, **B10**, 748 (1977).
181. G.Sh. Papava, I.S. Khitarishvili, S.V. Vinogradova, and V.V. Korshak, *Soobshch. Akad. Nauk SSSR*, 65, 345, 597 (1972); 68, 593 (1972).
182. S.V. Vinogradova, V.V. Korshak, K.A. Andrianov, G.Sh. Papava, and I.S. Khitarishvili, *Vysokomolek. Soed.*, A15, 1215 (1973).
183. V.V. Korshak, S.V. Vinogradova, G.Sh. Papava, and P.D. Tsiskarishvili, *Dokl. Akad. Nauk SSSR*, 156, 368 (1964).
184. L.B. Shirokova, I.P. Storozhuk, V.S. Voishchev, V.A. Beloglazov, V.S. Eremin, P.M. Valetsky, L.Z. Rogovina, G.L. Slonimsky, S.V. Vinogradova, and V.V. Korshak, *Vysokomolek. Soed.*, **A24**, 1974 (1982).
185. V.V. Korshak, T.A. Babushkina, V.A. Vasnev, S.V. Vinogradova, A.V. Vasil'yev, and G.K. Semin, *Isv. Akad. Nauk SSSR, Ser. Khim.*, 1921 (1970).
186. V.V. Korshak, S.V. Vinogradova, V.A. Vasnev, and A.V. Vasil'yev, *Polymer Letters*, 10, 429 (1972).
187. V.V. Korshak, S.V. Vinogradova, G.L. Slonimsky, A.A. Askadsky, A.V. Vasil'yev, V.A. Vasnev, K.A. Bychko, *Dokl. Akad. Nauk SSSR*, 199, 607 (1971).
188. V.V. Korshak, S.V. Vinogradova, V.A. Vasnev, E.B. Musaeva, A.P. Gorshkov, G.K. Semin, and L.N. Gvozdeva, *Dokl. Akad. Nauk SSSR*, 226, 350 (1976).
189. S.V. Vinogradova, V.A. Vasnev, V.V. Korshak, and T.I. Mitaishvili, *Vysokomolek. Soed.*, A11, 73 (1969); A12, 1108 (1970).
190. V.V. Korshak, V.A. Vasnev, M.G. Keshelava, S.V. Vinogradova, and L.N. Gvozdeva, *Vysokomolek. Soed.*, A20, 139 (1978).
191. V.M. Savinov and L.B. Sokolov, *Vysokomolek. Soed.*, 7, 772 (1965).
192. S.V. Vinogradova, V.A. Vasnev, E.I. Fedin, and V.V. Korshak, *Isv. Akad. Nauk SSSR, Ser. Khim.*, 1620 (1967).
193. V.V. Korshak, *Vysokomolek. Soed.*, A15, 298 (1973); A18, 1443 (1976); A19, 1179 (1977); A21, 3 (1979); *Usp. Khimii*, 42, 695 (1977).
194. S.A. Pavlova, in: *Polycondensation Processes and Polymers, Collected Papers*, Kabardino-Balkarsk University Press, Nal'chik, 1980, p. 134 (in Russian).
195. M.M. Koton, V.V. Kudryavtsev, V.P. Sklizkova, P.P. Nefedov, M.A. Lazareva, B.G. Belen'ky, I.A. Orlova, and S.Ya. Frenkel', *Vysokomolek. Soed.*, B22, 273 (1980).
196. V.V. Koršak, S.L. Rusanov, and L.Ch. Plieva, *Faserforsch. u. Textiltechnik*, 28, 371 (1977).
197. V.V. Korshak, A.L. Rusanov, and D.S. Tugushi, *Usp. Khimii*, 50, 2251 (1981).
198. A.L. Rusanov, in: *Polycondensation Processes and Polymers, Collected Papers*, Kabardino-Balkarsk University Press, Nal'chik, 1980, p. 188 (in Russian).
199. A.N. Pravednikov, in: *Polycondensation Processes and Polymers, Collected Papers*, Kabardino-Balkarsk University Press, Nal'chik, 1980, p. 5 (in Russian).
200. V.V. Korshak, A.L. Rusanov, C.G. Iremashvili, L.K. Plieva, and T.V. Lekae, *Makromol. Chem.*, 176, 1233 (1975).
201. V.V. Korshak, G.L. Berestneva, N.Sh. Ormotsadze, A.E. Chesnokova, M.P. Razmerova, A.L. Rusanov, A.M. Berlin, and N.G. Lekishvili, *Vysokomolek. Soed.*, A25, 634 (1983).
202. V.V. Korshak, E.S. Krongauz, A.M. Berlin, and P.N. Gribkova, *Dokl. Akad. Nauk SSSR*, 149, 602 (1963).

203. E.S. Krongauz, *Vysokomolek. Soed.*, **A26**, 227 (1984).
204. V.V. Korshak and A.L. Rusanov, *Vysokomolek. Soed.*, **A26**, 3 (1984).
205. V.V. Korshak, D.M. Mognonov, B.B. Tanganov, M.I. Batotsyrenova, V.V. Nikitaev, E.K. Batlaev, and A.A. Izyneev, *Vysokomolek. Soed.*, **A22**, 1209 (1980).
206. M.M. Koton, T.M. Kiseleva, G.I. Zhukova, S.N. Nikolaeva, L.A. Laius, and Yu. N. Sazanov, *Vysokomolek. Soed.*, **A23**, 1736 (1981).
207. V.V. Korshak, G.M. Tseitlin, and A.I. Azarov, *Vysokomolek. Soed.*, **B13**, 603 (1971).
208. V.V. Korshak, G.M. Tseitlin, O.S. Zhuravkov, F.B. Sherman, and V.A. Klimova, *Vysokomolek. Soed.*, **B16**, 99 (1974).
209. V.V. Korshak, S.V. Vinogradova, S.A. Siling, and I.I. Ponomarev, *Vysokomolek. Soed.*, **A23**, 1120 (1981).
210. S.V. Vinogradova, S.A. Siling, I.I. Ponomarev, and V.V. Korshak, *Vysokomolek. Soed.*, **A21**, 138 (1979).
211. V.V. Korshak, S.V. Vinogradova, and J.S. Vygodskii, *J. Macromol. Sci.-Rev. Macromol. Chem.*, **C11**, 45 (1974).
212. S.V. Vinogradova and Ya.S. Vygodsky, *Usp. Khimii*, **42**, 1225 (1973).
213. Ya.S. Vygodsky and S.V. Vinogradova, *Chemistry and Technology of High-molecular Compounds*, VINITI, Moscow, Vol. 7, 1975, p. 14 (in Russian).
214. V.A. Sergeev and V.I. Nedel'kin, *Vysokomolek. Soed.*, **A22**, 309 (1980).
215. V.A. Sergeev, V.K. Shitikov, V.I. Nedel'kin, and V.V. Korshak, *Vysokomolek. Soed.*, **A17**, 2420 (1975).
216. V.A. Sergeev, V.I. Nedel'kin, N.P. Ivanov, and A.V. Liven, *Vysokomolek. Soed.*, **B20**, 397 (1978).
217. V.V. Koršak, S.V. Vinogradova, and D.R. Tur, *Faserforsch. u. Textiltechnik*, 28, 339 (1977).
218. R.D. Katsarava, D.P. Kharadze, L.M. Avalishvili, and M.M. Zaalishvili, *Vysokomolek. Soed.*, **B24**, 198 (1982).
219. R.D. Katsarava, D.P. Kunchuliya, L.M. Avalishvili, and M.M. Zaalishvili, *Vysokomolek. Soed.*, **B21**, 643 (1979).
220. R.D. Katsarava, D.P. Kunchuliya, L.M. Avalishvili, G.G. Andronikashvili, and M.M. Zaalishvili, *Vysokomolek. Soed.*, **A21**, 2696 (1979).
221. V.V. Korshak, V.N. Kasatochkin, A.M. Sladkov, Yu.P. Kudryavtsev, and K. Usenbaev, *Dokl. Akad. Nauk SSSR*, **136**, 1342 (1961).
222. S.V. Vinogradova, and O.V. Vinogradova, *Usp. Khimii*, **44**, 1084 (1975).
223. S.V. Vinogradova, in: *Progress in the Synthesis of Organoelement Polymers*, Nauka, Moscow, 1966, p. 59 (in Russian).
224. S.V. Vinogradova and O.V. Vinogradova, in: *Progress in the Synthesis of Organoelement Polymers*, Nauka, Moscow, 1980, p. 10 (in Russian).
225. V.V. Korshak, S.V. Vinogradova, P.M. Valetsky, and N.I. Bekasova, *Vestn. Akad. Nauk SSSR*, No. 11, 23 (1974).
226. V.V. Korshak, V.A. Zamyatina, and N.I. Bekasova, *Organoboron Polymers*, Nauka, Moscow, 1975 (in Russian).
227. N.I. Bekasova and V.A. Zamyatina, in: *Progress in the Field of Organoelement Polymers*, Nauka, Moscow, 1980, p. 43 (in Russian).
228. A.A. Zhdanov, in: *Polycondensation Processes and Polymers, Collected Papers*, Kabardino-Balkarsk University Press, Nal'chik, 1980, p. 169 (in Russian).
229. N.I. Bekasova, *Usp. Khimii*, **53**, 107 (1984).

4 Synthesis of Polycondensation Polymers of Predetermined Structure

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1. INTRODUCTION

The fundamental problem of polymer science, associated with the production of high molecular weight compounds possessing the requisite combination of properties, has recently become especially relevant and given rise to an intensive search for ways to purposively control macromolecular structures. The solution of the problem at hand makes it possible to attain, in the course of synthesis, the desired sequence of units, including stereoisomeric units, in macromolecules, thereby enabling one to vary the properties of the resulting polymer in a delicate manner and in the right direction.

The problem involved is in turn directly related to one of the most general problems addressed by the chemistry of high molecular weight compounds, namely, the problem of raznozvennost' (different-unit structure). Formulated in the early 1970s by Korshak [1], the idea of raznozvennost' explicitly suggested the need, on the one hand, of making in-depth quantitative studies into macromolecular structures and of elucidating the nature and extent of effects of raznozvennost' on the properties of polymers, on the other. Considerable advances made in the modern theory and practice of polymer science and the great potential of current research techniques indicate that the problems under review can be coped with to advantage in the near future.

The synthesis of high molecular compounds with predetermined structures has assumed special importance for polycondensation polymers. Indeed, while for polymerization polymers numerous problems pertaining to directed control of their structures have been given much attention both in terms of theory and experimentation, then as far as polycondensation is concerned, no considerable progress has been made in this area until recently.

Such a situation has occurred because, in contrast to polymerization, a much wider range of starting compounds containing various functional groups can basically be used to synthesize polycondensation polymers. As a result, to prepare polymers with a particular set of properties, synthetic chemists first embarked on the path of

searching for novel monomers whose polycondensation allowed "constructing" macromolecules of different chemical nature, which, in the final analysis, enabled one to tackle specific applied problems. The exhaustion of the range of potential fairly available monomers and the production of high molecular weight compounds exhibiting various characteristics have given rise to a new task, viz. to find ways to purposefully combine individual fragments of macromolecules so that the properties of newly produced polymers would meet up-to-the-minute requirements.

Highly effective in this respect is the approach employing a variety of combinations of previously known monomers to prepare copolymers with a predetermined macromolecular unit distribution or, putting it another way, with a prescribed microstructure. The synthesis of random, regularly alternating, or block copolymers whose blocks vary in length is helpful not only in attaining the wanted combination of the particular characteristics of corresponding homopolymers; the direct varying of the microstructure of polymeric chains in the course of the reaction yields copolymers that are superior to "starting" polymer structures in their properties. The relevance and outlook of this approach have brought about rapid progress in research done in this area, which ultimately have established many basic principles underlying the synthesis of polycondensation copolymers with a specified microstructure.

The foregoing holds, to a large extent, true for "head-to-tail" polymers. The synthesis of such polymers involves monomers either with unsymmetrically located functional groups, e.g. monosubstituted hydroquinone, or with groups of varying chemical nature, say, amino alcohols. From the standpoint of polymerization, the above monomers have a "head" and a "tail", as it were. A combination of such monomers into macromolecules results in a special type of isomerism that is associated with the varying alternation of "heads" and "tails" along the chain.

Soviet polymer science has made important contributions to this work. The studies of Soviet workers on the synthesis of polycondensation polymers of prescribed structure, including both copolymers and "head-to-tail" polymers, are characterized by a balanced combination of theoretical research and experimentation. On the one hand, it imparts experimental reliability to theoretical works and serves as a dependable foundation for their development, while, on the other hand, it permits a considerable enhancement of the effectiveness of experimental studies into the synthesis of raznozvenny (different-unit) polymers exhibiting the desired set of properties.

2. THEORETICAL DESCRIPTION OF RAZNOZVENNOST' OF LINEAR POLYCONDENSATION POLYMERS

Statistical Characteristics of Raznozvenny Polymers. The availability of several types of units in macromolecules makes it more difficult to characterize such polymers than the species containing similar units. The knowledge of molecular-weight characteristics for raznozvenny polymers provides but a limited information on a polymer sample, since its properties depend also on the mole fractions of units of different type (composition) and their sequence distribution (structure). At the same time, the factor of raznozvennost' appreciably, and at times decisively, affects the set of physicochemical and mechanical properties of polymers [1]. This fact illuminates the importance of developing theoretical approaches with a view to quantitatively evaluating the degree of polymer raznozvennost' and establishing its dependence on the synthesis conditions. Hence, prerequisites arise to control the properties of polymeric products as early as the stage of their preparation.

The most common techniques of synthesizing raznozvenny polycondensation polymers are copolycondensation and the use of monomers with unsymmetrical units [1-3]. The former produces copolymers whose molecules are distinguished by the mode the units alternate in them, as in the case of the interbipolycondensation of two comonomers $A_1R_1A_1+A_2R_2A_2$ (say, glycols) with intercomponent BIB (say, dicarboxylic acid).

For theoretical and experimental purposes, it is easy and convenient to characterize the structure of the chains emerging in such a system of binary copolymers $\sim IR_1IR_1IR_2IR_1\sim$ by the coefficient of microheterogeneity, K_M, which is expressed in terms of fractions of different dyads of elementary units (R_1I) and (R_2I) (or the triads of monomeric units) using the relationship:

$$K_M = \frac{P(R_1R_2)}{P(R_1R_2)+2P(R_1R_1)} + \frac{P(R_1R_2)}{P(R_1R_2)+2P(R_2R_2)} \quad (1)$$

For a mixture of two homopolymers $P(R_1R_2)=0$ and, correspondingly, $K_M=0$, whereas for a regularly alternating copolymer $P(R_1R_1)=P(R_2R_2)=0$ and $K_M=2$. Between these two extreme cases corresponding to the ideally ordered arrangement of units in macromolecules all the possible values of K_M lie; in the case of complete random, that is, most disordered, unit distribution $K_M=1$. Consequently, the degree to which the microstructure has been ordered would be quantitatively avaluated from the absolute deviation of K_M from unity, while the deviation direction indicates the tendency of the monomeric units either to alternate regularly in the chains ($K_M>1$) or to form long blocks of the two comonomers ($K_M<1$). The task of

the theory is to express the fractions of dyads in terms of the kinetic (for non-equilibrium processes) or thermodynamic (for equilibrium processes) parameters of the system and then find the value of K_M using formula (1).

The microheterogeneity coefficient (formula 1) may also be employed to describe unit distribution in the products of bipolycondensation of monomers $A_1R_1B_1+A_2R_2B_2$ of the hydroxy acid type, each monomer is capable of producing a homopolymer in the process conditions.

The quantity K_M, as its definition implies, makes sense only for copolymers with two types of units. For this reason multicomponent copolymers, such as intercopolycondensation products with more than two types of comonomers $A_iR_iA_i$, ask for alternative ways of describing their microstructure. One of them involves assigning distribution function $f^{(i)}(n)$ according to the lengths of the n blocks of similar monomeric units $\sim R_iR_i\ldots R_i\sim$ of each ith monomer.

To provide an exhaustive description of unit distribution in a copolymer, one has to have an algorithm of finding probabilities, $P(U_K)$ (fractions), of any sequence U_K from any number of units, K. For arbitrary copolymers obtained via a polymerization mechanism, the problem in question was solved in 1962 by Price [4] who showed that macromolecules of such copolymers could be considered as individual realizations of a Markov chain. Their adequately developed mathematical theory enables one, using standard rules and simple algebraic operations, to express any probabilities $P(U_K)$ of the copolymer in terms of the parameters of the corresponding Markov chain. These parameters are, in a certain way, associated with the concentrations of monomers and their relative activities.

Participation of the monomers of unsymmetrical structure in polycondensation gives rise to an additional type of configurational isomerism, related to various ways by which the monomers involved enter the polymeric chain. This structural isomerism allowing for a mutual orientation of unsymmetrical units in the chain is possible even in homopolymers $\sim\vec{R}_IR_{II}\overleftarrow{R}_IR_{II}\vec{R}_IR_{II}\sim$ resulting from the heteropolycondensation of unsymmetrical $A_1\vec{R}_1A_2$ and symmetrical $B_1R_{II}B_1$ monomers. The raznozvennost' of the polymers thus yielded is similar to that observed in the case of the homopolymerization of vinyl monomers; however, in contrast, in polycondensation polymers, the portions of head-to-head and head-to-tail additions are normally comparable [3]. Such structural isomerism can be quantitatively characterized by the value of the direction coefficient K_D found from the formula similar to formula (1), where $(\vec{R}_I\overleftarrow{R}_I)$, $(\overleftarrow{R}_I\vec{R}_I)$, and $(\vec{R}_I\vec{R}_I)$ will be dyads. In meaning, a structural parameter K_D is closely related to the microheterogeneity coefficient since its

limiting values $K_D = 0$ and $K_D = 2$ comply with the block polymer $\sim(R_{II}\vec{R}_IR_{II}\vec{R}_I)_n\sim$ and the one that alternates along directions in the chain of unit $\vec{R}_I$, $\sim(R_{II}\vec{R}_IR_{II}\overleftarrow{R}_I)_n\sim$, that is, head-to-tail and head-to-head polymers.

Apart from the molecular-weight distribution, composition, and structure of raznozvenny polymers, they are also characterized by composition heterogeneity which is determined by the distribution of macromolecules according to composition, that is, the number of units of various types. This heterogeneity is responsible for some service properties of polymers, e.g. their transparency, and therefore its theoretical and experimental determination is of fundamental importance.

Kinetic Models and Calculation Techniques. To calculate the statistical characteristics of the configurational structure of raznozvenny polymers it is necessary to start from a particular kinetic model. The simplest and most common model is that of ideal polycondensation underlied by the principle of invariable reactivity. According to this principle, pioneered by Flory [5] and therefore named after him, the reactivity of any functional group does not vary in the course of polycondensation and remains equal to the value it had in the monomer. One of the possible causes responsible for the deviation of the system from ideality is what is known as "substitution effects" associated with steric, induction, and other types of effects exerted by the reacted functionalities on the activity of the unreacted neighbouring groups. In this case, reference is made to the first-order substitution effect ("the neighbouring group effect") if the reactivity of the group depends only on whether or not the group neighbouring it in the monomeric unit has reacted. When the reactivity of the group is affected by the state of the groups in the neighbouring units one has sometimes to take into account the substitution effects of higher orders of magnitude that are likely to occur. It stands to reason that the presence or absence of substitution effects is related directly to the structure of starting monomers.

To calculate statistical characteristics of the primary structure of non-equilibrium polycondensation products, two distinct approaches are followed, kinetic and statistical. The former involves formulating and solving material balance equations for concentrations of all types of molecules participating in the process in question. The latter calculates mole fractions of molecules with assigned configurations, available among all other constituents of the reaction mixture. These fractions are identified with the probability that a randomly selected molecule has a corresponding configuration. There are various options of applying the statistical approach to calculating the said probabilities, and several options can be used simultaneously to describe the same polymer.

The statistical method of calculating polycondensation processes was first put forward by Flory as early as the 1930s [5] and then found the most extensive application in quantitatively characterizing a large number of both linear and branched polymers. The principal advantage of the statistical method is that it allows for an exhaustive and relatively simple description of the detailed configurational structure of macromolecules in terms of several probability parameters. The statistical method, however, is essentially formal in that the foundations for describing the products of a specific nonequilibrium polycondensation system can be presented only within the framework of the kinetic approach. The latter, furthermore, allowed expressing the corresponding probability parameters appearing in the formulas employed by the statistical method in terms of kinetic constants, reactant concentrations, and other quantities being measured.

To validate rigorously whether a particular modification of the statistical approach is applicable to describing the primary configurational structure of equilibrium polycondensation products, it is necessary to employ the general approach to statistical thermodynamics. For instance, in equilibrio, the probabilities of the synthesis of different macromolecules in the system are defined by changes in its free energy due to the formation of all their intramolecular bonds and, as the principle of detailed balance implies, are independent of the sequence in which these bonds have appeared, that is, of the system's genesis. Based on the general thermodynamic relations, express changes in the free energy can be expresed during the formation of intramolecular bonds in terms of equilibrium constants of the corresponding elementary reactions that conform to the stoichiometric scheme of the process under review. This allows relating them directly to probability parameters employed in the statistical approach.

Stages in the Development of Quantitative Theory. A Soviet scientist, Shtraikhman [6], appears to be the first to have classified copolycondensation processes and deduced the equation relating conversions of comonomer functionalities in the course of ideal irreversible interbipolycondensation. Based on this equation, the study [7] was made into the dependence of the copolymer composition on conversion for varying ratios of the starting monomers and the relative activity of their functional groups. With certain values of stoichiometric parameters, a similar problem was solved numerically by Polish workers [8-10] and Sokolov *et al.* [11]. In the last work, calculation was made of the composition of a copolymer arising from a mixture of comonomers gradually added to the intercomponent at different rates of their introduction into the reaction zone. The task of calculating the composition of equilibrium interbipolycondensation products was coped with in the work [12] where its relationship

with thermodynamic parameters was established.

The composition of a copolymer resulting from the irreversible process was calculated for the intercopolycondensation of any number of comonomers [13, 10] as well as for the bipolycondensation of monomers $A_IR_IB+A_2R_{II}B$ [14].

In all the works cited above, the authors proceeded from the model of ideal polycondensation. For this reason, of special interest is a theoretical analysis of the interbipolycondensation of monomers with dependent functional groups [15]. On the basis of the general kinetic scheme of the "neighbouring group effect" model for all three monomers, Sokolov *et al.* [15] derived a system comprising six kinetic equations for the concentrations of all the functional groups, yet, they came up with not quite accurate coefficients because of the improper selection of stoichiometric factors.

Calculations of various average molecular weights, their distribution, and distribution of polycondensation copolymer molecules by size, composition, and functionality (SCFD) can be made using both statistical [16-18] and kinetic [19-21] methods. Specifically, Case [16] developed formulas for molecular-weight distribution (MWD) as well as for the weight-average and number-average molecular weights of ideal bipolycondensation products, while theoretical studies [17, 18] were made into the ratio of these quantities but for the case of a copolymer yielded by ideal interbipolycondensation. General formulas derived by Kuchanov and Pis'men [19] make it possible, using elementary algebraic operations, to come up with analytical expressions for the generating functions of SCFD of arbitrary ideal copolycondensation products, and from them, using standard methods, to find distributions themselves and their statistical moments. The above workers [20] have formulated a general algorithm which enables the distribution in question to be calculated in a similar fashion for copolycondensation involving monomers with dependent groups.

The problems of theoretically establishing unit distribution in polycondensation copolymers were tackled in varying detail. The distribution concerned can be most easily characterized by the fractions of different dyads of units, which in the case of a binary copolymer, given its composition, are defined only by the value of the microheterogeneity coefficient (formula 1). The characteristic for the products of irreversible interbipolycondensation was calculated in Soviet studies [21-23], and that for bipolycondensation products was dealt with in the former of them. Kuchanov [21] showed that if the intercomponent alone has independent functional groups, then unit distribution in the copolymer chain will invariably be completely random. This finding arises from the equality $K_M=1$, which holds true irrespective of the ratio of activities and proportions of comonomers as well as of conversion. The same author [21] investi-

gated theoretically the effects of the above factors on the quantity K_M in the opposite case when comonomers have independent groups whereas the intercomponent reacts in compliance with a simplified "neighbouring group effect" model. According to the model involved, the activity of the intercomponent second group located at the end of any polymer molecule is independent of the type of the comonomer penultimate unit but differs from the first group activity. Such a model is characterized by merely four rate constants of elementary reactions, of which one can develop three dimensionless ratios defining the relative reactivities of various functional groups. The number of these kinetic parameters drops to two when assumption is made (as in Ref. [15]) of proportionality of the activities of the intercomponent first and second groups during their reaction with various comonomers. Within the framework of such a simplified "neighbouring group effect" model, Kuchanov [21] brought out the basic patterns of the relationship between the microheterogeneity coefficient and the system's stoichiometric and kinetic parameters and derived simple analytical formulas for K_M for various limiting values of these parameters. Similar findings for equilibrium interbipolycondensation were obtained in the work [24] where it was proved, among other things, that independence of the intermonomer groups is a sufficient condition to prepare a completely random copolymer.

The kinetic calculation of K_M for irreversible interbipolycondensation products [21] indicates that the nature of the chain microstructure is primarily governed by the mutual dependence of the reactivities of functional groups in the intercomponent. If they are independent, then, according to theory, $K_M=1$ and unit distribution at any conversion, any ratio of comonomers and their activities will invariably be completely random. The nature of changes in the reactivity of functional groups in the intercomponent during their reaction with comonomers has been found to agree generally with the nature of unit distribution in the copolymer. If, on entering of the intercomponent first groups into a reaction, the activity of the second groups decreases, then, in this case, the chain units should exhibit a tendency to alternate ($K_M>1$); otherwise, when the activity of the second groups increases, a tendency to form blocks ($K_M<1$) should become apparent. For one and the same intercomponent with dependent groups, the ordering of the copolymer microstructure increases with increasing variations in the activities of comonomers.

A theoretical analysis of irreversible [21] and equilibrium [25, 26] bipolycondensation pioneered by Soviet workers had demonstrated that this process has some qualitative features discriminating it from interbipolycondensation, the most important feature consisting in the fact that even in the model of ideal bipolycondensation,

$A_1R_1B_1+A_2R_2B_2$, K_M turns out to be, generally speaking, different from unity.

A specific characteristic of non-equilibrium polycondensation fundamentally distinguishing it from the equilibrium process is the possible dependence of some statistical characteristics of its products on the manner of introduction of the starting monomers into the reaction zone. Kuchanov [22] was the first to establish the theoretical correlation between K_M and the relative activities of the monomers on their gradual introduction into the reaction zone and also on irreversible interbipolycondensation conducted by various multistage methods. For example, in the case when the intercomponent is added sufficiently slowly, so that the rate of its introduction into the reaction zone is low as compared with the rate of entering of its groups into the reactions, a simplified model of the "neighbouring group effect" gave [22] a straightforward analytical expression for the microheterogeneity coefficient. It follows from this expression that the structure of the formed copolymer is independent either of the rate of supply of the intercomponent (provided it is sufficiently low) to the reaction zone or of the relative activities, $\varkappa$, of its first and second groups. Since the thus determined value of K_M is always less than unity, the unit distribution will tend to the formation of blocks whose length depends, for a given composition, only on the relative activity, r, of comonomers. The stronger their reactivities differ, the less is K_M and hence the larger the average length of blocks in the copolymer. Some of the formulas derived by Kuchanov [21, 22] were later obtained in an independent study [23].

The second method of an approximate description of the microstructure of linear copolymers consists in assigning the distribution functions of similar units with the length of blocks. The first calculations of these functions for the products of ideal intercopolycondensation of a stoichiometric mixture of monomers were made by Beste [13]. Using the statistical method, the author found that for each type of units, R_i, the distribution is geometric (Flory) with a parameter $\alpha_i p_i^2$ depending only on the initial mole fraction (α_i) of a corresponding ith comonomer, $A_iR_iA_i$, and the conversion (p_i) of its functional groups, A_i. In contrast to this case (a completely statistical copolymer) Kuchanov [22] has solved a similar problem within the framework of a simplified "neighbouring group effect" model for the intercomponent. The solution of corresponding kinetic equations gives, in line with the earlier findings [13], a geometric distribution whose parameter is, however, expressed through the concentrations of the dyads of units and turns into $\alpha_i p_i^2$ on condition of the independence of intercomponent's functional groups. A statistical analysis of the distribution of units with the length of blocks in the products of ideal irreversible interbipolycondensation of a non-stoichiometric mixture was carried out by Gritsenko [27, 28]. The author conducted

a qualitative theoretical study of the effect of the stoichiometry and activity of the starting monomers on the character of distribution of units for a single- and two-step process mode. The latter case has been analysed [29] to give the polydispersity (distribution) coefficient, $f^{(i)}(n)$ of blocks, i.e. the ratio of the weight-average and number-average block lengths of the ith comonomer as a function of the stoichiometry, conversion, and also relative activities of the first and second groups of the intermonomer. Various average block lengths were also calculated by the authors referred to above [13, 22, 27, 28].

For an exhaustive description of the distribution of units in a copolymer, an algorithm of the calculation of the probability of their arbitrary random sequence is needed. A comparatively simple algorithm of this kind is available for linear copolymers whose configurational statistics is Markovian. In this context the paper [30] is of general significance for the quantitative theory because it indicates that the products of an arbitrary homogeneous process of ideal irreversible copolycondensation are described by a Markov chain with parameters related in a certain manner to the constants of elementary reactions and to the ratios of the starting monomers. A similar result for equilibrium ideal copolycondensation was obtained in the work [24]. It was also noted that any order of "substitution effects" which was taken into account in the theory does not disturb the Markovian character of unit distribution in the copolymer. The same authors employed different versions of the "neighbouring group effect" model for calculating the parameters of a corresponding Markov chain in the ultimate case when the average polymerization degree is $P_N \to \infty$. In order to find these parameters, the authors derived a set of simple algebraic equations and found its analytical solution for interbipolycondensation. The expressions for the parameters under discussion given in Ref. [33] at arbitrary P_N make it possible to perform calculations of polycondensation processes giving rise to reactive oligomers which often serve as precursors of commercial synthesis of polymers. These conclusions are only an illustration of the results provided by the general formulas for the parameters of the Markov chain [33], which describes the configurational statistics of the products of arbitrary equilibrium copolycondensation within the framework of the "neighbouring group effect" model for all monomers. The Markovian character of this statistics in the same system but for non-equilibrium copolycondensation conditions has not been proved yet. Moreover, it seems that such a proof is impossible in principle for systems which are not quasi-ideal. The quasi-ideality condition for intercopolycondensation consists in the independence of functional groups either in the intercomponent or in all comonomers. In the first case, even when the "neighbouring group effect" model acts in the comonomers, the distribution of units in the macro-

molecules will follow the Bernoulli statistics [31] and in the second, the first-order Markov chain. This result and the parameters of the chain were first obtained for a simplified "neighbouring group effect" model [31] and after that, for its full version [32].

The finding of an unambiguous correlation between the configurations of the copolymer molecules and the examples of a certain Markov chain made it possible to obtain [24, 30, 31] simple asymptotic formulas for the composition distribution functions of polycondensation copolymers at large P_N. In the case of interbipolycondensation considered in Refs. [24, 30, 31] these distributions are Gaussian and depend only on three parameters: P_N, the composition of the initial mixture of monomers, and microheterogeneity coefficient, K_M. An analysis of these dependences shows that the composition distribution becomes narrower with growing P_N and with the decreasing degree of blocking in the copolymer (K_M rising).

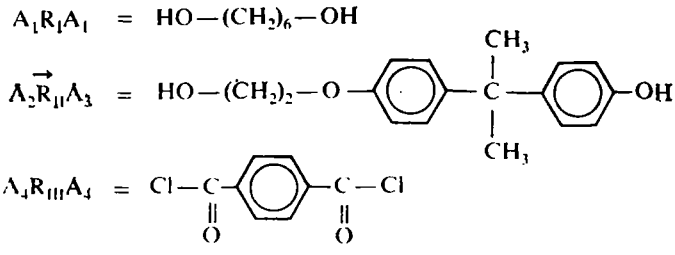
The methods offered by Markov chain theory allow calculating any required characteristics of the primary structure of linear copolymers including their molecular-weight distribution. A series of papers by Durand and Bruneau [34-38] was dedicated to this problem, as applied to different polycondensation systems. Their results, although obtained by rather intricate reasoning, constitute only special cases of formulas reported in the earlier works [19, 20].

The paper [39] concerning homopolymers formed in the course of irreversible heteropolycondensation with the participation of a monomer containing unsymmetrically located functional groups is closely related to the copolycondensation theory. Two types of addition of monomers to the chain are possible in the polymers of this kind: "head-to-head" ("tail-to-tail") and "head-to-tail". It was demonstrated [39] that the statistical description of such polymers, with the type of addition of units taken into account, can follow the formulas of the interbipolycondensation theory developed by Kuchanov [21, 22].

In order to describe raznozvennost' of more complex polycondensation polymers, such as polymers containing more than one type of unsymmetrical units or multicomponent copolymers, a further generalization and development of the theoretical approaches put forward in the papers referred to above are required. The main ideas of these improved approaches worked out by us quite recently are expounded in the following paragraph.

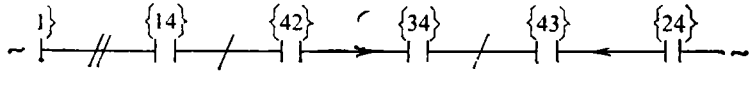
The Fundamentals of Describing Raznozvennost' of Polycondensation Polymers. One of the specific features of polycondensation polymers is the variety of the types of links joining the monomer units; this fact should be taken into consideration in describing the microstructure of macromolecules. The chemical structure of polymer chains can be represented in abbreviated form as a sequence either of monomer units or of links. A fragment of a copolymer molecule obtained by interbipolycondensation of two diols with

isophthaloyl chloride (System 2)



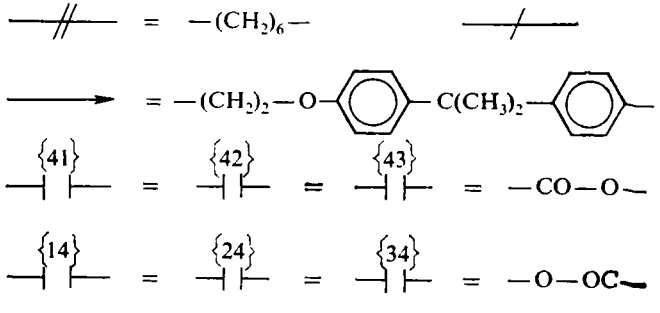
(2)

is depicted by the following scheme:



(3)

The segments with marks on them refer to different monomer units and parallel vertical dashes on their ends, to links:



(4)

Chemically identical functional groups, e.g. hydroxyls in System 2, may differ kinetically in relation to the type of their reactivity in the monomer. The groups in a symmetrical monomer are always of the same type (e.g. A_1 or A_4) and in an unsymmetrical one they are, as a rule, of different types (A_2 and A_3). It is convenient to assume that any group A_i is contained only in one monomer. Similarly, chemically identical internal functional groups (links) are to be distinguished by types (*ir*) with respect to the reaction of a pair of groups, A_i and A_r, producing them. For instance, ester links of different types are shown in Scheme 4. Pairs (*ir*) and (*ri*) denote the same link type. This link type, in schematically representing the molecules or their fragments, corresponds to two different pairs, $\{ir\}$ and $\{ri\}$, in which the order of succession of symbols i and r is essential. Thus, the ($\{41\}\{14\}$) fragment contains the R_I unit

surrounded by R_{III} units and the ({14}{41}) fragment, on the contrary, the R_{III} unit surrounded by R_I.

Each molecule can conventionally be represented in a manner reflecting its structural formula (see Scheme 3). By this method the location of figures and symbols of monomer units can be indicated in the only possible way. It can easily be seen that the structural formula of a molecule can be reestablished if one knows only the sequence of the $\{ir\}$ pairs on its schematic picture (3) because the dashes and the direction of the arrows on the segments depicting the monomer units are determined unambiguously. Hence, the fragment of the polymer chain shown in Scheme (3) can be represented as a sequence of "directed links":

$$\sim\{1\}\{14\}\{42\}\{34\}\{43\}\{24\}\sim \qquad (5)$$

This method of notation is particularly convenient in the case of unsymmetrical monomer units when it is not sufficient to indicate only their sequence in the polymer chain but the orientation of units should be specified, e.g. with the help of arrows. Then the same fragment of the molecule will be represented as $\sim R_I R_{III} \vec{R}_{II} R_{III} \overleftarrow{R}_{II} R_{III} \sim$.

In Scheme (5), the dyad of directed units is shown as a single (ir) link joining the units. For instance, the {34} link corresponds to the $\vec{R}_{II}R_{III}$ dyad of monomers in System (2). The proportion of the (ir) links, $P(ir)$, among all possible links coincides with the probability of a corresponding dyad. Similarly, the probability of a triad generated by the central unit of monomer $A_iR_vA_l$ coincides with the probability, $P(\{ri\}\{js\}) \equiv P(\{sj\}\{ir\})$, of the pair of neighbouring links equivalent to it. The experimentally measured probabilities, $P(ir)$, $P(\{ri\}\{js\})$, are related between themselves and to the composition of the monomer mixture through stoichiometric dependences which can be used in NMR spectroscopic data processing. For example, they can be useful in signal assignment, separation of overlapping peaks, or adjustment of less reliable data on the basis of more exact ones.

The first group of dependences links the probabilities of dyads and the initial concentrations μ_i^0 of A_i groups relative to one monomer unit, the concentrations being determined by the mole fractions, $\alpha_v \equiv \alpha_{(ij)}$, of monomer $A_iR_vA_j$ in the initial mixture:

$$\sum_r (1+\delta_{ir})\,P(ir) = \mu_i^0 + (1+\delta_{ij})\,\alpha_{(ij)} \qquad (6)$$

where $\delta_{ij}=1$ at $i=j$ and $\delta_{ij}=0$ at $i\neq j$. Some of Eqs. (6), each of them corresponding to a certain type, i, of groups, can be expressed through the others. To determine the number of independent parameters

$P(ir)$, one should subtract the rank of the set of linear equations (6) from their total number.

Another group of dependences relates the probabilities of the triads between themselves and to the proportions of the dyads. To obtain them, consider triads generated by monomer units $A_iR_vA_j$ and $A_rR_uA_n$. If their concentrations are known, one can find the concentrations of the (ir) links by two methods. If all the concentrations are taken with respect to one monomer unit, the following relationship between the probabilities of dyads and triads will emerge:

$$\sum_s (1+\delta_{ij}\delta_{rs})\, P(\{ri\}\{js\}) = (1+\delta_{ir})\, P(ir) =$$

$$= \sum_m (1+\delta_{rn}\delta_{im})\, P(\{ir\}\{nm\}) \qquad (7)$$

If the (ir) link is symmetrical, i.e. $i=r$, then both equations (7) are equivalent. In order to find the number of independent linear equations among Eq. (7), one needs to know, as in the case of Eq. (6), the rank of the matrix of this system. This procedure will give the minimum total number of parameters necessary for the description of configurational statistics on the level of dyads and triads.

However, the choice of the parameters is not unambiguous. For instance, the necessary number of independent proportions of triads, $P(\{ri\}\{js\})$, can be taken as parameters. But this is not the most successful choice because it is difficult to draw a direct conclusion about the character of the microstructure of the polymer on the basis of the values of the parameters. The alternative choice is based on the analogy with the microheterogeneity coefficient, K_M, whose minimum and maximum values ($K_M=0$ and $K_M=2$) reflect the ultimate structures: block and alternating binary copolymers. It is only reasonable to seek similar structure parameters for more complex systems so that their extremum values would characterize specific microstructures of corresponding polymers. The magnitude of these parameters could be used to make a judgement about trends in raznozvennost' of macromolecules.

The structure parameters depending only on the probabilities of dyads naturally make up an individual group. Their number coincides with the number of independent $P(ir)$ values, which is sufficient for the analysis of dyad distribution. To describe the statistics of triads, additional parameters are required, their number being determined by the rank of the set of linear equations (7).

Yet another division of the parameters into two groups naturally emerges when copolymers with two types of isomerism are described. The first group refers to the order of sequence of units with

"erased" arrows indicating their directions. The remaining parameters concern the correlations of these directions within such sequences "without arrows", $R_\nu R_\mu \ldots R_\varkappa$. If the parameters of one of the groups are specified, then certain restrictions can be imposed on the possible values of the other parameters since the ultimate microstructures corresponding to the extremum values of different parameters can be conflicting. Similar restrictions on the combined ranges of allowable values are also possible for parameters belonging to the same group. The character of the restrictions defines the shape of the variation range of possible values of structure parameters.

These parameters specify exhaustively the microstructure of raznozvenny polymers when it is described by Markovian statistics. Thus, it was shown [30, 24] that the probability parameters of the Markov chain pertaining to the products of random ideal copolycondensation are expressed via the proportions of different dyads of directed monomer units. On copolycondensation of monomers with dependent groups, the onset of equilibrium, at least in exchange reactions, is sufficient for Markov copolymers to emerge; here chain propagation and termination can occur in a non-equilibrium mode. If all the reactions proceed in an irreversible manner, then the Markov chain theory is applicable only to "quasi-ideal" systems in which any monomer unit with dependent groups can be joined only to monomers whose functional groups are kinetically independent [32]. In order to estimate raznozvennost' of polymers which are formed in such quasi-ideal systems not only the concentrations of dyads but also the proportions of triads generated by monomer units with dependent groups are to be specified. These quantities are also unambiguously related to the structure parameters proposed by us. Hence, on the assumption of the Markovian statistics of the polymer its raznozvennost' can be fully calculated on the basis of the values of the structure parameters. The method of selection of these parameters and the description of the features of configurational statistics of polymers with their help are shown below using a concrete system as an example.

An Example of Selection of Structure Parameters. Consider interbipolycondensation of System 2 monomers. Due to the unsymmetrical nature of one of the comonomers, the copolymer formed features two types of isomerism simultaneously. One of them, as in the case of ordinary interbipolycondensation of symmetrical monomers, is related to the character of alternation of units R_I and R_{II} and the second one, to the orientation of the directions of monomer unit $\vec{R}_{II}$ in the chain.

The proportions of different dyads, $P(ir)$, are fully defined by the composition of the initial monomer mixture

$$P(14)=2\alpha_I, \quad P(24)=P(34)=\alpha_{II}, \quad \alpha_I+\alpha_{II}=\alpha_{III}=0.5 \qquad (8)$$

Hence, all structure parameters of this particular system are related to the distribution of triads. Each comonomer unit generates one triad, the proportions of the triads being evidently α_I and α_{II}. The probabilities of six triads generated by one intermonomer unit will be denoted as $P_{rs} \equiv P(\{r4\}\{4s\})$:

$$P_{11} = P(R_I R_{III} R_I), \quad P_{12} = P(R_I R_{III} \vec{R}_{II}), \quad P_{13} = P(R_I R_{III} \overleftarrow{R}_{II})$$

$$P_{22} = P(\overleftarrow{R}_{II} R_{III} \vec{R}_{II}), \quad P_{23} = P(\vec{R}_{II} R_{III} \vec{R}_{II}), \quad P_{33} = P(\vec{R}_{II} R_{III} \overleftarrow{R}_{II})$$

For these values to be assigned, three parameters are sufficient since there exist three stoichiometric conditions (9):

$$2P_{11} + P_{12} + P_{13} = P(14), \quad P_{12} + 2P_{22} + P_{23} = P(24)$$

$$P_{13} + P_{23} + 2P_{33} = P(34) \tag{9}$$

It is quite natural to choose microheterogeneity coefficient

$$K_M = 2\,\frac{P(R_{III})\,P(R_I R_{III} R_{II})}{P(R_I R_{III})\,P(R_{II} R_{III})} = \frac{P_{12} + P_{13}}{4\alpha_I \alpha_{II}} \tag{10}$$

describing the isomerism of the sequence of R_I and R_{II} units as the first among these structure parameters.

Here K_M has the same sense as the microheterogeneity coefficient in interbipolycondensation of symmetrical monomers and defines, as is specified by formula $L^v = 1/(1-2\alpha_v)\,K_M$, the average lengths, L^v, of blocks $(R_v R_{III})$ of comonomer units. However, full characterization of the copolymer structure also calls for a description of the order of sequence of $\vec{R}_{II}$ units in blocks $(R_{II} R_{III})_n$.

These blocks can be represented as the fragments of a homopolymer furnished by heteropolycondensation of a symmetrical and an unsymmetrical monomer. Its microstructure is defined by the only parameter, direction coefficient K_D. It is therefore reasonable to introduce in the case under analysis a similar structure parameter,

$$K_D = 2\,\frac{P(\overleftarrow{R}_{II} R_{III} \vec{R}_{II}) + P(\vec{R}_{II} R_{III} \overleftarrow{R}_{II})}{P(R_{II} R_{III} R_{II})} = 2\,\frac{P_{22} + P_{33}}{P_{22} + P_{33} + P_{23}} \tag{11}$$

Its value characterizes the distribution of "arrows" of $\vec{R}_{II}$ units in the $(R_{II} R_{III})_n$ blocks. Each of the blocks can consist of several clusters. A continuous sequence of m identically oriented elementary units, $(\vec{R}_{II} R_{III})$, limited either by units of opposite orientation or by

edges of the blocks, will be named a cluster of length m. The number-average length of the cluster is determined, as is shown below,

$$L_C = 2/[K_D + 2\alpha_I K_M (2 - K_D)] \qquad (12)$$

only by structure parameters, K_M and K_D, which also make it possible to find the average number of clusters in one block:

$$L^{II}/L_C = 1 + K_D(1 - 2\alpha_I K_M)/4\alpha_I M_M \qquad (13)$$

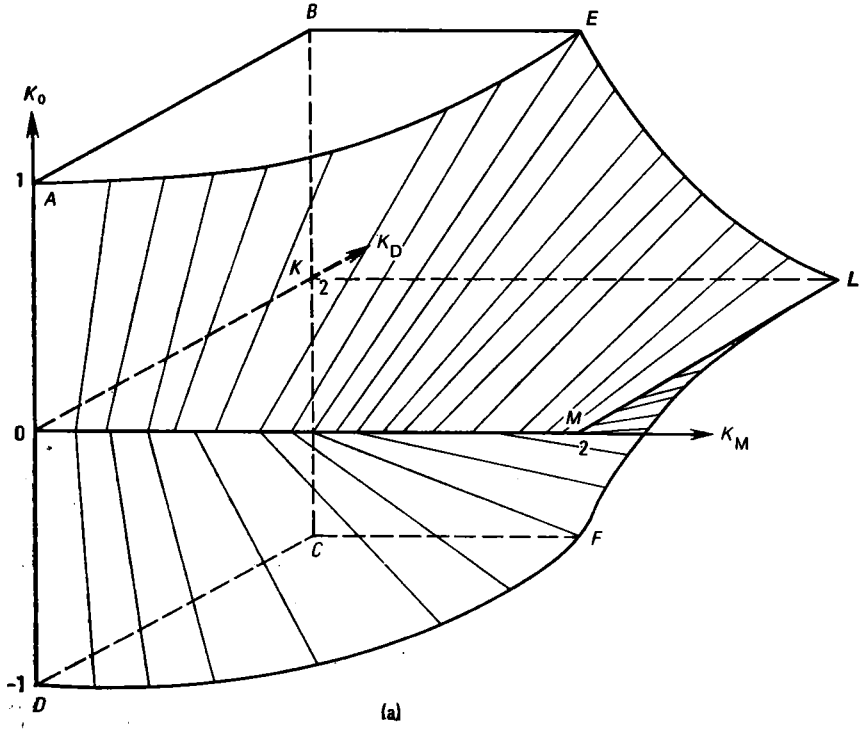
With K_D decreasing, the average length of clusters grows and in the limit (K_D=0) one block contains exactly one cluster. Alternatively, the growth of K_D testifies to the increase in the average number of clusters in a block, i.e. to the trend towards alternation of the "arrows". The maximum value of the parameter (K_D=2) corresponds to blocks of the $(\vec{R}_{II}R_{III}\overleftarrow{R}_{II}R_{III})_n$ type with all clusters of unit length.

The value of the direction coefficient describes fully, on the triad level, the raznozvennost' of the homopolymer with $(\vec{R}_{II}R_{III})$ elementary units. However, K_D alone proves to be insufficient for representing the block microstructure of these units in the interbipolycondensation products. This difference is due to the fact that a homopolymer always has $P_{22}=P_{33}$ while in a copolymer the probabilities of the "head-to-head" (P_{33}) and "tail-to-tail" (P_{22}) orientations of two neighbouring $\vec{R}_{II}$ units may be unequal because of the orientation of the terminal clusters of the block. Thus, a full description of the microstructure of the copolymer under consideration on a triad level necessitates the use of a new parameter, e.g. orientation coefficient

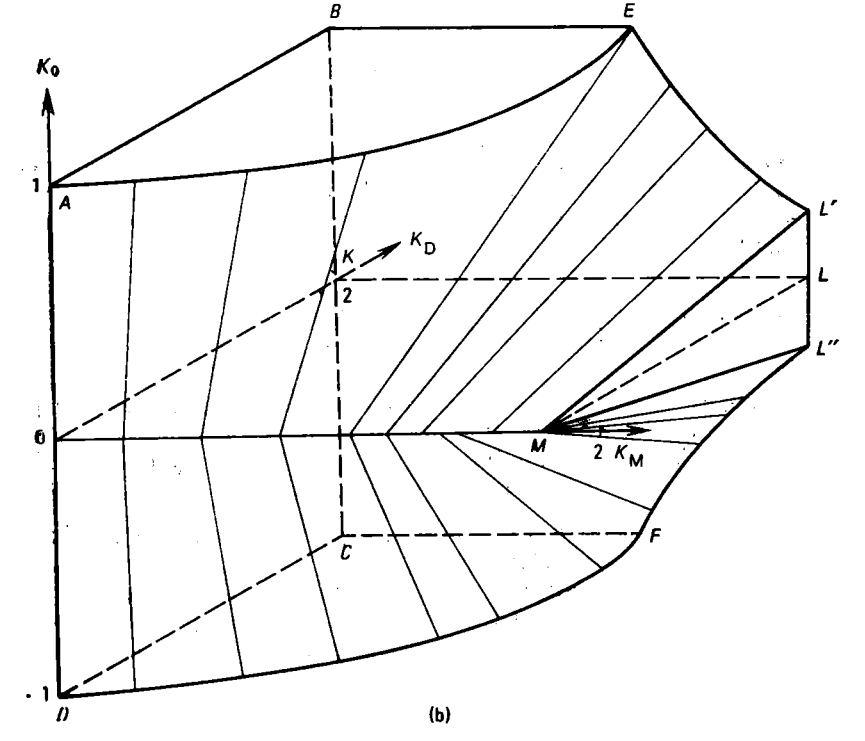
$$K_o = \frac{P(R_IR_{III}\vec{R}_{II}) - P(R_IR_{III}\overleftarrow{R}_{II})}{P(R_IR_{III}R_{II})} = \frac{P_{12} - P_{13}}{P_{12} + P_{13}} \qquad (14)$$

in addition to K_M and K_D. This structure parameter shows the prevailing orientation of the terminal cluster inside ($K_o > 0$) or outside ($K_o < 0$) the block. Its modulus, $|K_o|$, quantitatively characterizes these trends so that the ultimate values of K_o ($K_o = 1$ and $K_o = -1$) refer to blocks whose terminal units, $\vec{R}_{II}$, are oriented only inside and only outside, respectively.

A detailed analysis gives rise to a set of inequalities defining the area of acceptable values of the triplet of structure parameters. The shape of the area depends on the composition of the starting monomer



(a)



(b)

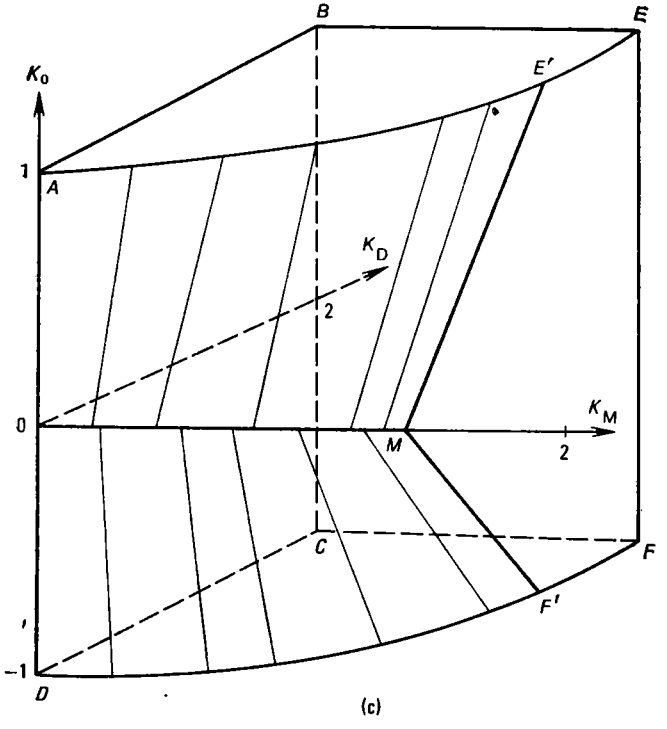


Fig. 1. The range of variation of structure parameters characterizing the raznozvennost' of a copolymer obtained by interbipolycondensation of monomers (System 2) at different ratios: (a) $\alpha_I = \alpha_{II}$, (b) $2\alpha_I > \alpha_{II} > \alpha_I$, (c) $\alpha_{II} > 2\alpha_I$

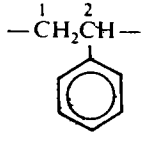
mixture, as can be seen from Fig. 1. The location of the point corresponding to a copolymer sample in this diagram speaks of the character of raznozvennost' of the sample.

3. EXPERIMENTAL DATA ON THE SYNTHESIS OF POLYCONDENSATION POLYMERS OF A DEFINITE MICROSTRUCTURE

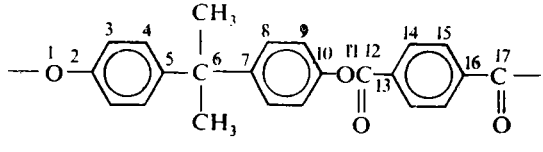
Historically, the circumstances turned out so that equilibrium, reversible, polycondensation was studied first; in this field much has been done by Korshak and his school [40]. Only later the change to more active monomers served as a basis of investigating into irreversible, non-equilibrium, polycondensation. A thorough analysis of the kinetics, mechanism, and the main principles governing the reaction made it possible in the 1960-1970s to arrive at a

sufficiently full understanding of non-equilibrium polycondensation and, first of all, of non-equilibrium low-temperature polycondensation [41]. Low-temperature polycondensation carried out under mild conditions is not accompanied by back and exchange degradation reactions, this feature favouring the conservation of the microstructure of polymer chains formed in the course of synthesis and making a sound basis for the use of the low-temperature polycondensation method for preparing polymers of a specified structure. It is not surprising therefore that the overwhelming majority of studies in this field, including those carried out by Soviet researchers, deal with low-temperature non-equilibrium polycondensation.

The intense development of current physical methods and their application to the analysis of the structure of high-molecular compounds is another factor contributing to a substantial progress in the synthesis of polycondensation polymers of a predetermined microstructure. Here the first place undoubtedly belongs to high-resolution NMR spectroscopy, one of the main methods of polymer physics and chemistry. At the onset of the development of NMR spectroscopy, mostly vinyl type carbon-chain polymers were the subject of research. The switch of heterochain polycondensation polymers was hampered by the potentialities of the NMR method which were limited at that time. Indeed, a comparison of a carbon-chain polymer, polystyrene (I), and a heterochain polymer, polyarylate (II), shows quite clearly that in going from the former to the latter the number of atoms in the main chain of the base unit increases from 2 to 17.



I



II

Thus, judging by the number of atoms in the main chain, one unit of polyarylate contains over eight polystyrene units. This example shows that much improvement of NMR spectroscopy is required in studying the character of distribution of base units in the macromolecules of heterochain polymers as compared with carbon-chain polymers. Refinements in the method, such as the development of ^{13}C NMR spectroscopy, were sound prerequisites for a successful application of NMR spectroscopy in quantitative analysis of raznozvennost' of polycondensation polymers and a reliable foundation of polycondensation syntheses of high-molecular compounds of a specified structure.

The fundamentals of the use of NMR in identifying the structure of carbon-chain and heterochain polymers are on the whole invariable and have been discussed in detail in numerous monographs (see e.g. Ref. [42]). Therefore, this point will not be touched upon in the present review.

3.1. Copolymers

Equilibrium Polycondensation. In 1967 the first paper on the quantitative determination of the microstructure of polycondensation copolymers was published; the paper dealt with copolyesters synthesized by equilibrium copolycondensation of glycols with dimethyl esters of dicarboxylic acids in melt. Yamadera and Murano [43] found that under these conditions random copolymers are formed, parameter K_M being equal to 0.90-1.03. The authors convincingly showed that interchain exchange reactions can be one of the reasons of this phenomenon. Indeed, heating of a mixture of two homopolymers, polyethyleneterephthalate and polyethylenesebacate, at 270 °C for 3 h gave a random copolymer because of ester interchange.

Starting from 1968, Soviet researchers Slonim, Urman, and others [42, 44-48] successfully used NMR spectroscopy in determining the composition and structure of copolyesters, including unsaturated copolyesters obtained by equilibrium copolyesterification. Quantitative determinations of the microstructure of such copolymers showed that their structure was random or close to it.

In 1971 Hongo *et al.* [49] found that polyneopentylterephthalatesebacate synthesized by equilibrium copolyesterification in melt is a random copolymer.

Chelate europium compounds were in 1972 successfully used in determining the structure of polyethyleneterephthalateisophthalate [50]. The values of K_M calculated, as a function of composition, from the data provided by this paper differ only slightly from unity, i.e. the structure of the copolyesters is close to random.

Studies carried out by Hamb *et al.* [51, 52] are of much significance for the understanding of the processes occurring in equilibrium copolycondensation; the authors found that the heating of a polyester, dicarboxylic acid, and bisphenol diacetate gives rise to a random copolymer because of exchange reactions.

In this context, of particular interest is the paper [53] published in 1982 and concerning the analysis of the microstructure of copolyimides by ^{13}C NMR.

The specificity of the process of synthesis of copolyimides consists in that at high temperatures the formation of polyamidoacid is reversible whereas at temperatures close to room temperature the decomposition of polyamidoacid does not take place almost at all.

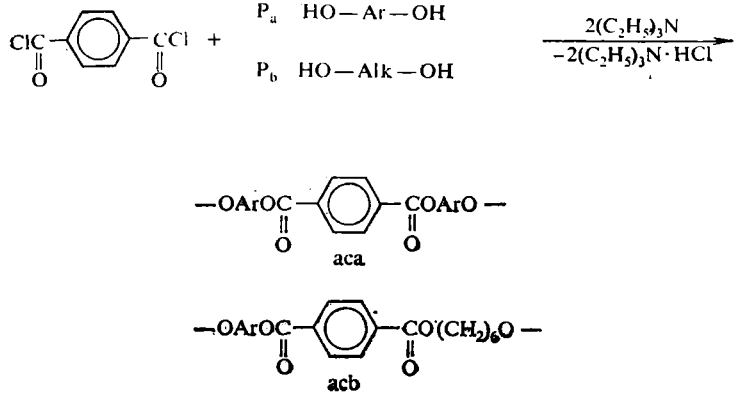
As a consequence, only random copolyimides can be obtained, regardless of large differences in the activities of diamines and other conditions, on running the whole process in one step at 200 °C because of the reversibility of the formation of polyamidoacids. The authors were able to prepare copolyimides of block structure only by the synthesis and cyclization of polyamidoacids at 20 °C [53].

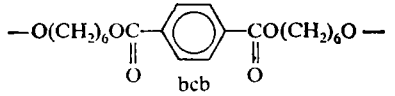
Thus, until now copolymers only of random structure or sufficiently close to random have been obtained, in conformity with the theory, under the conditions of equilibrium copolycondensation due to back and exchange degradation.

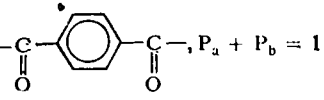
Non-equilibrium Copolycondensation. It has already been emphasized that the main difference between non-equilibrium and equilibrium polycondensation consists in the irreversibility of the former with respect to low molecular weight products and, as a rule, in the absence of interchain exchange reactions [41]. These features create necessary prerequisites for retaining the polymer microstructure formed at the synthesis stage which, in turn, is a necessary condition of producing a polymer of a specified structure.

Homophase Systems. In 1972 first reports dealing with the regularities of the formation of copolymer microstructure during non-equilibrium copolycondensation appeared in the literature. Korshak, Vinogradova, Vasnev, *et al.* [54, 55] studied the effect of the reaction conditions and of the activity of comonomers on the composition and structure of copolyesters. Further development of the experiments and the combination of experimental results with theoretical findings made it possible to formulate the basic principles of the formation of copolymer macromolecules under the conditions of non-equilibrium copolycondensation in solution [2, 56].

Copolyesters prepared by acceptor-catalytic interbipolycondensation in solution were chosen as subject of research:





where a = —OArO—, b = —O(CH$_2$)$_6$O—, c =  , $P_a + P_b = 1$

Important results were obtained in studying the microstructure of copolymers synthesized by copolycondensation in one stage, i.e. under conditions when at the very beginning of the reaction all monomers were in solution [54, 56-59]. It was found that the structure of macromolecules formed under these conditions is close to random and depends only slightly on the difference in the reactivities of comonomers (Table 1, Compounds 1 and 3). The determinations of the composition and structure of the copolymers in the course of copolymerization showed that at the beginning of the process the copolymer is enriched in units containing a more active comonomer; however, further on the proportion of the units becomes equal to the initial ratio of comonomers. Eventually, when the reaction is completed, the composition of the high molecular weight compound produced is identical with the composition of the initial mixture. In contrast to composition, parameter K_M remains practically unchanged throughout the whole process with its value indicating that random copolymers are formed. This result proved the fallibility of the viewpoint widespread at that time according to which non-equilibrium copolycondensation of comonomers with different activities should give rise not to random but to block copolymers (see e.g. Ref. [60]). In reality it was found that the difference in the activities of comonomers results only in that the composition of macromolecules changes as non-equilibrium copolycondensation proceeds while the character of distribution of units remains unchanged and close to random.

Copolymers with the statistical distribution of units were also synthesized under two-stage copolycondensation conditions representing an infinitely large difference in the activities of comonomers (Table 1, Compounds 2 and 4). By this method, the second comonomer was introduced into the reaction zone only after polycondensation of the intermonomer with the first comonomer had ceased [54, 58, 59, 61]. Experiments showed that a slight deviation from the random distribution of units in the macromolecules (K_M values, as shown in Table 1, vary between 1.09 and 1.28 whereas for the random copolymer K_M=1) is caused by a decrease of the activity of the second COCl group of terephthaloyl chloride (intermonomer) after the first COCl group has entered into the reaction [56].

It turned out that the necessary condition of the formation of block copolymers in one- and two-stage copolycondensation in solu-

Table 1. The Structure of Copolyterephthalates Obtained from Bisphenol and Hexamethyleneglycol by Acceptor-Catalytic Copolyesterification in the Presence of Triethylamine (Dichloroethane, 40 °C)

No.	Bisphenol	Reactivity of ratio comonomers, r	Concentration of triads, mole fractions			K_M
			aca	acb	bcb	
1	Bis(4-hydroxy-3-methylphenyl)-2,2-propane*	5.3	0.19	0.62	0.19	1.24
2	Same**	∞	0.19	0.64	0.17	1.28
3	Bis(4-hydroxy-3-chlorophenyl)-2,2-propane*	33	0.22	0.56	0.22	1.12
4	Same**	∞	0.25	0.54	0.21	1.09

* Triethylamine (0.4 mole/litre) was added to a solution of terephthaloyl chloride (0.2 mole/litre), bisphenol (0.1 mole/litre), and hexamethyleneglycol (0.1 mole/litre); copolyesterification time was 1 h [59].

** Triethylamine (0.4 mole/litre) was added to a solution of terephthaloyl chloride (0.2 mole/litre) and bisphenol (0.1 mole/litre). 30 min later, hexamethyleneglycol (0.1 mole/litre) was introduced into the reaction mixture and the reaction was continued for 1 h [61].

tion is gradual introduction of the intermonomer into the reaction zone [55, 59]. When the intermonomer (terephthaloyl chloride) is introduced in solid form, the gradualness is caused by the rate of its dissolution. However, the amount of the intermonomer can be controlled more reliably and easily by feeding its solution into the reaction zone at a known rate.

It was found that on a gradual introduction of the intermonomer into the reaction zone the growth of the reactivity ratio (difference in activity values) of the comonomers increases the length of the blocks and hence decreases K_M (Table 2). With the duration of the introduction of the intermonomer growing, the microheterogeneity coefficient of the copolyester decreases tending to its ultimate value defined by the reactivity ratio of the comonomers [59].

Together with one- and two-stage copolycondensation, the three-stage method can be used for the synthesis of block copolymers [59]. The principle of three-stage copolycondensation consists in that polycondensation of each comonomer with the intermonomer is carried out in different reaction volumes. After the end of the reactions in each of the systems, they are joined which starts copolycondensation between the macromolecules formed at the first stages. The intermonomer is taken in excess with respect to the comonomer in one system and in deficiency in the other so that the total mole quantities of the functional groups of the intermonomer and comono-

Table 2. The Structure of Copolyterephthalates Obtained from a Bisphenol and Hexamethyleneglycol by Single-stage Copolyesterification in the Presence of Triethylamine on Gradual Introduction of Terephthaloyl Chloride into the Reaction Solution (Dichlorpethane, 40 °C) [55]

Bisphenol	r	Length of blocks		K_M
		n_{ac}	n_{bc}	
Bis(4-hydroxy-3-methylphenyl)-2,2-propane	5.3	4.4	4.4	0.46
9,9-Bis(4-hydroxyphenyl)-fluorene	12.6	5.6	5.6	0.36
Bis(4-hydroxy-3-nitrophenyl)-2,2-propane	31.0	8.2	8.5	0.24
Bis(4-hydroxy-3-chlorophenyl)-2,2-propane	33.0	9.2	9.2	0.22

mers were equal. The length of blocks in the copolymer is determined by the deviation of the proportion of the functional groups from equivalence at the first two stages; the lowest value of the microheterogeneity coefficient of the copolymer was achieved on the nearest approach to the equivalence between the intermonomer and the comonomers at the first stages.

An analysis of experimental data and the development of theoretical studies enabled the Soviet researchers [2, 3, 56] to formulate the main regularities of the formation of the microstructure of copolymer macromolecules under non-equilibrium copolycondensation conditions in a homophase system:

1. The introduction of the whole amount of the intermonomer into the reaction zone at once at the beginning of non-equilibrium interbipolycondensation leads, regardless of the difference in the activities of the comonomers, to the formation of random copolymers. The use of a bifunctional compound with dependent functional groups as intermonomer affects the microstructure of the copolymers; the decrease in the activity of the second functional group after the first one has entered into the reaction raises the proportion of regularly alternating fragments in the polymer chains while the increase in the activity of the second functional group of the intermonomer is conducive to the growth of the length of blocks.

2. A stepwise introduction of the comonomers into the reaction zone is not a sufficient condition of the synthesis of copolymers of block structure.

3. To synthesize block copolymers by single-stage non-equilibrium polycondensation in a homophase system, it is essential that the comonomers should differ in activity and the rate of supply of the

intermonomer into the reaction zone be lower than the rate of its interaction with the more reactive comonomer.

Varying the above-mentioned factors, one can obtain block copolymers with different lengths of blocks, thus controlling the microstructure and properties of macromolecules of copolymers in a desired manner [59].

These experimental data covering the effect of different factors on the composition and structure of copolymers produced by non-equi-

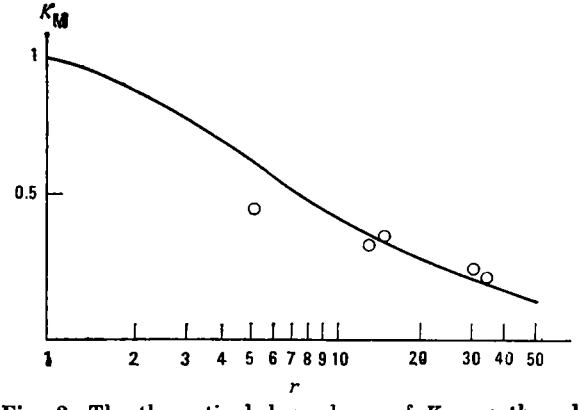


Fig. 2. The theoretical dependence of K_M on the relative activity of comonomers, r, on the gradual introduction of the intermonomer (○ : experimental points) [56].

librium copolycondensation in a homophase system are in good agreement with the basic conclusions of the kinetic theory of non-equilibrium interbipolycondensation developed by Kuchanov *et al.* [56, 62]. Adequate quantitative fit of the theory to the experiment (Figs. 2 and 3) shows that the conclusions based on the results of copolyesterification studies are of a general nature and reliably describe the regularities of the formation of the microstructure of copolymer macromolecules under the conditions of non-equilibrium copolycondensation in a homophase system.

The experimental data appeared in the 1970s fully agree with the disclosed principles.

In 1973 Curnuck and Jones [63] determined by PMR spectroscopy the structure of aromatic copolyamides prepared in different solvents. It was found that the addition of solid isophthaloyl chloride to a solution of diamines in tetramethylenesulphone in a two-stage process gives rise to copolymers of block structure with K_M in a 0.10-0.56 range. Rapid mixing of the reactants at the first stage, as could be expected, leads to the formation of a copolyamide with $K_M=1.26$.

Mackoy *et al.* [64] in 1978 showed with the help of PMR spectroscopy that on one- and two-stage acceptor-catalytic copolyesterifi-

cation, the addition of the comonomers (diphenylolpropane and neopentylglycol) to the intermonomer (terephthaloyl chloride) solution brings about the formation of copolyesters with a microstructure close to random. The same study demonstrated that the reactivity of the second COCl group of the intermonomer, after the first one had entered into the reaction with the alcohol, decreased to about 1/3

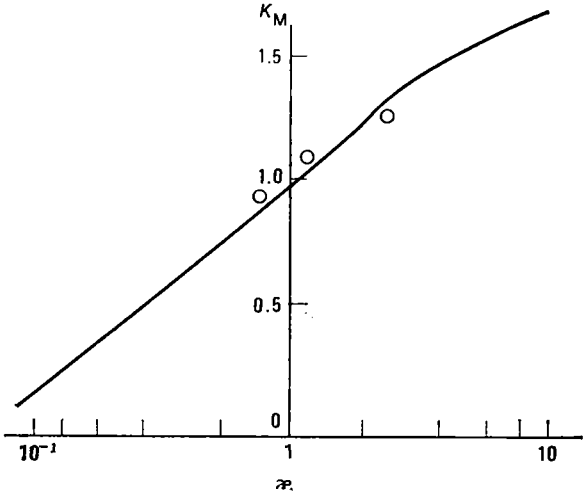


Fig. 3. The theoretical dependence of K_M on the variation degree of the activity of functional groups in the intermonomer, $\varkappa$, on two-stage copolycondensation (○: experimental points) [56]

of the initial level. Under the conditions of a two-stage process, this favours the formation of a copolymer with $K_M=1.38$, i.e. with a noticeable contribution of regularly alternating structures.

In 1979 Turska *et al.* [65] showed using an example of single stage high-temperature copolycondensation of terephthaloyl chloride with dimethyldian and phenolphthalein that, depending on the reaction temperature affecting the difference in the activities of bisphenols, copolyarylates with $K_M=0.87—1.00$ are formed, which implies that their structure is close to random.

In conclusion, it is worthwhile mentioning once again the experiments of Korshak *et al.* [53] who in 1982 studied the influence of the synthesis conditions on the microstructure of copolyimides. It was found that when the process is run at room temperature (i.e. in the non-equilibrium copolycondensation mode), the addition of a solid intermonomer (dianhydride) to the solution of comonomers (diamines) leads to the formation of copolymers of block microstructure with $K_M=0.40$.

Heterophase Systems. At present, aqueous-organic systems are the most common type of heterophase polycondensation systems widely used in interphase polycondensation processes. Interphase polycondensation has provided a large number of various copolymers: copolyamides, copolyarylates, copolycarbonates, polyamidoesters, etc. During recent 10-15 years, many regularities of this process have been scrutinized from every point of view. However, most of the authors of these studies first aimed at determining the composition of copolymers whereas scarce attempts at establishing their structure were as a rule based on indirect data. Not until quite recently not only the composition but also the microstructure of copolymers have been defined reliably.

One of the first experiments of this kind was carried out by Hongo, Suzuki *et al.* [49] in 1971. The authors found by PMR spectroscopy that interphase copolycondensation of ethylene glycol bischloroformate, diphenylolpropane, and ethylene diamine gave polyurethane carbonates with microstructure close to random (K_M=0.86-0.95).

In 1976 Gouinlock *et al.* [66] used PMR spectroscopy to show that two-stage interphase copolyesterification of terephthaloyl chloride, diphenylolpropane, and neopentylglycol yields a random copolymer with K_M=1.

In 1978 Ogata *et al.* [67] reported the results of an investigation of anhydrous interphase interbipolycondensation of isophthaloyl chloride with *m*- and *p*-phenylenediamines. The authors carried out copolycondensation in two immiscible organic solvents, e.g. ethylene glycol and acetonitrile, in the presence of organic (tertiary amines) or inorganic (alkali) bases. It was found that the nature of the solvents has actually no effect on the molecular weight, composition, and microstructure of the copolyamides formed. For instance, PMR spectroscopic data indicate that irrespective of the type of the solvents and bases used, copolyamides with the microheterogeneity coefficient ranging between 0.71 and 0.86 are formed. The same authors obtained copolyamides with K_M=0.80 from these monomers under aqueous interphase copolycondensation conditions. These results testify to the formation, in different heterophase systems, of random block copolymers with very short blocks.

Ogata *et al.* [67] also demonstrated that aqueous interphase copolycondensation gives, depending on the nature of the organic solvent, copolyamides with K_M varying from 0.80 to 1.02. K_M was found to drop with the polarity of decreasing organic medium.

Raigorodskii, Slonim, Urman *et al.* [69] in 1978 studied single-stage heterophase (interphase and emulsion) copolycondensation of piperazine with diphenylolpropane and oligosiloxane bischloroformates and found that on rapid introduction of the intermonomer solution into the reaction system, copolymers with K_M=0.63-0.78 are formed, i.e. copolymers of block microstructure with short blocks. The

authors attribute this result to the heterophase nature of the system.

Continuing the studies of non-equilibrium copolycondensation in a homophase system mentioned above, Korshak *et al.* [70-73] in 1981-1982 carried out a systematic investigation into non-equilibrium copolycondensation in an anhydrous heterophase system. Copolyesters produced by heterophase acceptor-catalytic copolyesterification of aromatic dicarboxylic acid chlorides (intermonomers) with such comonomers as bisphenol and glycol (see Eq. 15) or with two different bisphenols were chosen as the subject of investigation. In the course of synthesis, the copolymers formed precipitated from the reaction solution.

The investigations showed that the microstructure of copolymers obtained on the addition of triethylamine to the solution of starting monomers strongly depends on the nature of the organic medium. The variation of the amount of *n*-heptane (strong precipitating agent) in its mixture with acetone, dichloroethane or toluene makes it possible to change K_M of copolyesters in a rather broad range: from 0.8 to 1.3 [71]. Under similar conditions but in a homophase system, the use of solvents strongly differing in their properties, e.g. dichloroethane and dioxane, has practically no effect on K_M of copolymers (K_M=1.12 and 1.09) [2].

Extensive studies of the properties of the solvents used and of their mixtures demonstrated that this phenomenon is caused by the different ability of the organic media to precipitate copolymers from solution and to bring about their swelling which, in the final analysis, affects the stage of growth of macromolecules during heterophase copolycondensation. For example, it was found that an increase in the precipitating capacity of a mixture of acetone with *n*-heptane diminishes K_M of copolyesters (see Fig. 4) [70-71].

In contrast to homophase copolycondensation, the heterophase process features the growth of K_M of copolymers with an increase in the concentration of monomers in solution. Therefore, higher concentrations of the reactants and the growth of the precipitating capacity of the organic medium set up conditions favouring the formation of block copolymers [71].

The same authors disclosed that on single-stage copolycondensation in a heterophase system, as in the case of the homophase process, a gradual introduction of the intermonomer (acid chloride) into the reaction solution facilitates the formation of copolymers of block microstructure [73]. However, in contrast to homophase copolycondensation, the heterophase conditions of the process level off the effect of the relative activities of the comonomers (diols) on the length of the blocks formed and on K_M of copolyesters.

Studies of the influence of the synthesis conditions and relative reactivities of bisphenols on the composition and structure of copolyarylates demonstrated that on heterophase non-equilibrium co-

polycondensation the main regularities of the formation of the microstructure of copolyarylates and aryl aliphatic polyesters are similar [72].

An analysis of these results makes it possible to conclude that the regularities of the formation of the microstructure of copolymers under the conditions of heterophase non-equilibrium copolycondensation, unlike homophase copolycondensation, cannot be generalized without reservations. The reason of this situation lies in the fact

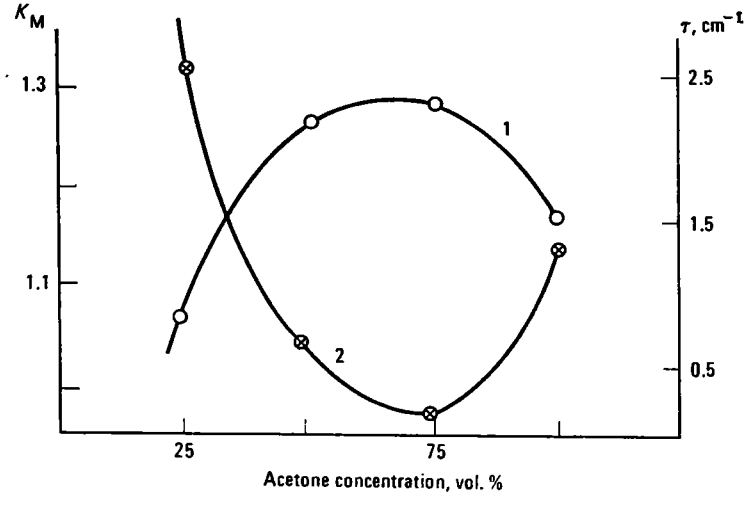


Fig. 4. The dependence of K_M of a copolyterphthalate obtained from dichlorodiphenylolpropane and hexamethyleneglycol (*1*) and of the precipitating capacity of the medium (*2*) on the composition of an acetone/*n*-heptane mixture (τ is turbidity for volumetric proportion of the precipitating agent, 0.45) [71]

that the process of formation of copolymers in a heterophase medium is complicated by the action of diffusion and other factors inherent in such systems. Nevertheless, it is the action of these factors that is responsible for the keen interest in heterophase copolycondensation because it enables the structure of copolymers to be varied in a broad range. It seems that the finding of the general principles of formation of copolymer microstructure in a heterophase process is a very complicated and important task which calls for supplementary theoretical and experimental studies.

3.2. "Head-to-Tail" Type Polymers

On polycondensation of monomers with an unsymmetrical location of functional groups, a problem of the determination and control of the microstructure of polymer chains formed arises. If one of the two monomers has an unsymmetrical structure, then the sequence of chemical bonds in the macromolecule may follow two patterns: "head-to-head" ("tail-to-tail") and "head-to-tail":

$$\begin{array}{l}(\ldots -\underset{\text{"head-to-tail"}}{ab-c-ab-c-ab-c-ab-c-}\ldots \\ x-c-x+y-ac-y \rightarrow \\ \ldots -\underset{\text{"head-to-head" ("tail-to-tail")}}{ba-c-ab-c-ba-c-ab-c-}\ldots\end{array} \qquad (16)$$

The number of versions grows to eight if both monomers are unsymmetrical. Optical activity of the initial compounds strongly enhances the complexity of the task of determining the microstructure of macromolecules.

If copolymers are regarded as structures similar to polycondensation polymers obtained from a symmetrical and an unsymmetrical starting compounds where the symmetrical monomer acts as intermonomer and the functions of the unsymmetrical component are distributed among the comonomers, it can be assumed that the general trends in the formation of the microstructure of such high-molecular compounds should be similar. Hence, under equilibrium polycondensation conditions, exchange and reverse reactions will set up prerequisites for obtaining polymers with a statistical location of "heads" and "tails" along the chain. On the other hand, under mild conditions of non-equilibrium polycondensation, the synthesis can be carried out in a desired direction to give polymers of a specified microstructure and with predetermined properties by varying the parameters of the reaction.

An analysis made by Kuchanov *et al.* [39, 62, 74] shows that the kinetic scheme of polycondensation involving an unsymmetrical monomer and hence its mathematical description coincide with that applied in calculating copolycondensation.

Equilibrium Polycondensation. One of the first papers dealing with polycondensation polymers of the "head-to-tail" type was published by Izard [75] who in 1952 reported about the results of studies of polyesters synthesized by equilibrium polycondensation of unsymmetrical dicarboxylic acids and glycols. X-Ray diffraction analysis revealed the prevalence of the "head-to-tail" addition. However, the author believes that these results concerning the

microstructure of the high-molecular compounds cannot be regarded as reliable because X-ray diffraction analysis gives information only about their crystalline portion.

Several years later Doak and Campbell [76] determined melting temperatures and crystallinity degree for several types of polyesters containing substituents either in the acid or in the glycol units which allowed the researchers to draw qualitative conclusions about the microstructure of the polymers. The authors believe that irregular addition of "heads" and "tails" occurring under the conditions of equilibrium polycondensation in melt gives rise to a random structure of copolyester and therefore to the growth of the defectiveness of crystal lattice and to the lowering of the melting temperature.

In 1957 Sogomonyants and Volkenshtein [77] studied stereoisomerism in polyesters and polyamides obtained by equilibrium polycondensation from optically active monomers containing "heads" and "tails". This study was the first to touch upon the problem of the stereochemical structure of polycondensation high-molecular compounds synthesized from optically active unsymmetrical monomers and demonstrated substantial influence of microstructure on the physical properties of the polymers considered.

Simultaneously with them, Korshak *et al.* [78-80], taking high-temperature polycondensation of monoethanolamine with dicarboxylic acids, provided a reliable proof of the equilibrium character of the process giving rise to polyamidoesters uniform in their chemical composition and molecular weight and apparently random in their microstructure.

It can be suggested that it is because of exchange and reverse reactions resulting in the random structure of macromolecules that the literature does not contain any data on the synthesis of polymers of this type with a specified microstructure and, generally, any quantitative information on their structure.

Non-equilibrium Polycondensation. Many papers dedicated to the synthesis of "head-to-tail" polymers under non-equilibrium polycondensation conditions have been published. The absence of exchange and reverse reactions in this case opened up a way of preparing high-molecular compounds with a predetermined structure and a desired set of properties. However, up to 1974 [39] no clear-cut proof of the character of polymer microstructure or its quantitative description has appeared in the literature.

One of the first investigations in the field of low-temperature non-equilibrium polycondensation with the participation of unsymmetrical monomers was that of Panayotov [81] on the synthesis of polyamidoesters published in 1963.

In 1966 Preston *et al.* [82] obtained new thermally stable fully aromatic polyamides based on isomeric diaminobenzanylides and

dicarboxylic acid chlorides under the conditions of low-temperature polycondensation carried out either in an interphase process or in solution with acid chloride introduced the last into the reaction zone. The authors noted that the unsymmetrical character of the benzanylide monomer capable of entering the polymer chain in two ways, "head-to-head" ("tail-to-tail") or "head-to-tail", carries in itself the possibility of the irregularity in the structure of macromolecules. A comparison of the melting temperatures and solubilities of the polymers thus obtained with those of earlier described random and regular polyamides [83] showed that the former occupy an intermediate position in their properties. A conclusion was made that in the case of a strong difference in the reactivities of the functional groups of the unsymmetrical monomer, the formation of a regularly built polymer containing the "head-to-head" ("tail-to-tail") sequences should be expected [82]. Polyamides synthesized by the authors on the basis of diaminobenzanylides were named "limited order" polymers.

Culbertson and Murphy [84, 85] also class their fibre-forming polyamidohydrazides with "limited order" polymers.

Almost simultaneously with Preston, several authors published their results of the use of unsymmetrical monomers in preparing polyester- and polyamidohydrazides [86] and polyamides [87, 88] and ascribed certain structures to the polymers in a very arbitrary manner.

After 1966 when the idea about "limited order" polymers was put forward, Preston *et al.* [89-95] in a series of publications analyse in detail some features of the formation of their microstructure, possible methods of its investigation, and the dependence of the physical properties of fibre- and film-forming polymers on their structure. Preston's studies undoubtedly belong to fundamental investigations in the field of polycondensation high-molecular compounds based on unsymmetrical monomers and deserve much attention although, as was noted above, the author analyses the structure of these polymers using only indirect data which casts doubt on the reliability of the main ideas developed by him.

At the beginning of the 1970s a large number of papers appeared informing about the synthesis of "head-to-tail" type polymers and qualitatively evaluating the microstructure of macromolecules. Thus, polycarbonateureas [96], polyamidoesters [97, 98], polysulphonamides [99], and a number of other polymers [100-102] were obtained from monomers of unsymmetrical structure under non-equilibrium polycondensation conditions. In fact, the authors of the papers did not consider the possibility of control of the polymer microstructure by varying the conditions of synthesis.

In 1974 Korshak, Vinogradova, Vasnev, Markova, *et al.* [39] for the first time reported about the synthesis of polymers from

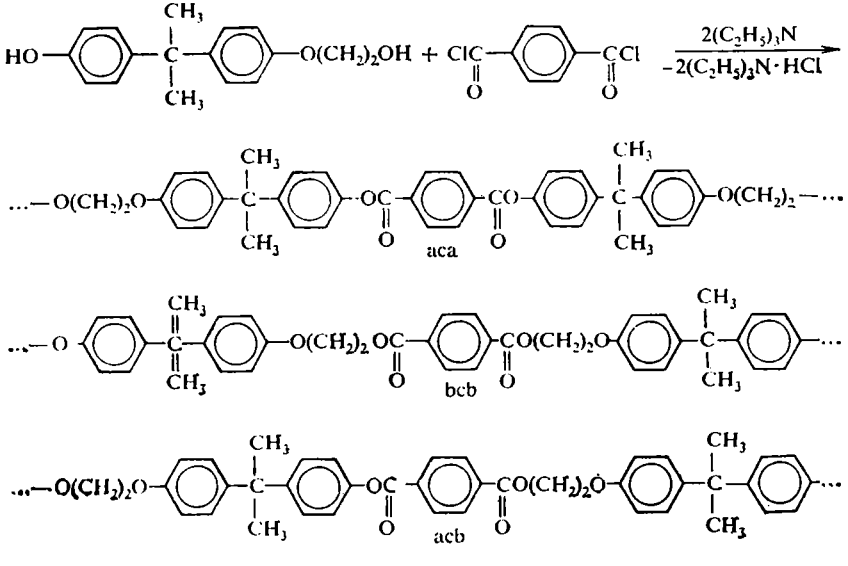
unsymmetrical monomers; the microstructure of the polymers was quantitatively described with the help of NMR spectroscopic data. Further experiments in this direction revealed the main regularities of the formation of the microstructure of polymers of the "head-to-tail" type under the conditions of non-equilibrium polycondensation [103-106].

The experiments dealt with polyesters prepared by acceptor-catalytic polycondensation of symmetrical (x—c—x) and unsymmetrical (y—ab—y) starting compounds in homophase and heterophase systems in the presence of triethylamine. Chlorides of dicarboxylic acids served as symmetrical monomers and mono-β-hydroxyethyl ethers of bisphenols, dioxybenzene, and naphthol, as unsymmetrical reactants:

$$\mathrm{ClC(O)-Ar-C(O)Cl + HO-Ar'-OCH_2CH_2OH} \xrightarrow[-2(C_2H_5)_3N\cdot HCl]{2(C_2H_5)_3N} \rightarrow \ldots\mathrm{-C(O)-Ar-C(O)-Ar'-OCH_2CH_2O-}\ldots \quad (17)$$

("head" — "tail")

The polycondensation of an unsymmetrical monomer, y—ab—y, with a symmetrical one, x—c—x, gives rise to polymer chains which may contain both the aca and bcb sequences resulting from the "head-to-head" and "tail-to-tail" additions and the acb and bca sequences caused by the "head-to-tail" and "tail-to-head" additions. In the case of terephthaloyl chloride and 4,4′-diphenylolpropane-2,2 (dian) mono-β-hydroxyether, these sequences can be depicted as follows:



The relative concentrations of the aca, bcb, and acb sequences found by NMR were used to calculate microheterogeneity coefficients, K_M, which, as was shown above, quantitatively characterize the regularity of the structure of macromolecules.

Two patterns of the introduction of the starting compounds into the reaction sphere were employed. The first pattern involved a gradual introduction of a symmetrical monomer (dicarboxylic acid chloride) into the solution of an unsymmetrical monomer and triethylamine. In one case acid chloride was rapidly added in solid form (method A) so that the rate at which it entered the reaction zone was determined by the rate of its dissolution and in another, a solution of acid chloride was introduced into the reaction zone for a predetermined period of time, τ (A^{τ} method). The second pattern involved the dissolution of monomers in an organic solvent with polycondensation started after the introduction of the whole amount of triethylamine into the reaction mixture (method B). Using different solvents, the authors carried out polycondensation in homophase (dichloroethane, dioxane) and heterophase (acetone) systems [103, 105]. Some of the results obtained in the experiments are summarized in Table 3.

Table 3. The Dependence of the Structure of Polymers Obtained in Different Media on the Method of Introduction of the Starting Compounds into the Reaction Sphere [103, 105]

ClC(=O)–C6H4–CCl(=O) + y—ab—y, where y—ab—y is	Method of introduction of monomers*	K_M		
		Dichloroethane	Dioxane	Acetone
HO–C6H4–C(CH3)2–C6H4–O(CH2)2OH, r = 16	A	0.77	0.85	0.84
	A^{15}	0.60	0.39	0.49
	B	1.02	1.01	0.92
HO–C6H4–C(CH3)2–C6H4–O(CH2)2OH, r = 22	A	0.68	0.64	0.74
	A^{15}	0.62	0.29	0.65
	B	1.11	1.12	1.09

Note: r is the relative activity of OH group in diols [105].
* The superscript shows the duration of the introduction of a solution of acid chloride or triethylamine in minutes.

It can be seen from Table 3 that polycondensation of dian and dichlorodian mono-β-hydroxyethyl ethers with terephthaloyl chloride, if both components are present in solution (method B), gives polymers with unit distribution close to random ($K_M \approx 1$). In other words, under these conditions even a considerable difference in the reactivities of phenolic and alcoholic diol OH groups does not bring about the formation of polymers of regular structure. This result has proved the fallibility of the existing viewpoint according to which the difference in the activities of the functional groups of the unsymmetrical monomer is the sufficient condition of the preferential addition of the diol residues in a "head-to-head" ("tail-to-tail") manner ($K_M < 1$). A slight deviation of K_M from unity ($K_M > 1$) observed in the experiment indicates, as Korshak *et al.* believe, the reduction of the activity of the second COCl groups of corresponding dicarboxylic acid chlorides after the first ones have entered into the reaction [39, 103, 105].

It was found that only gradual introduction of the symmetrical dichloride into the reaction sphere makes it possible to employ the difference in the activities of the functional groups of the unsymmetrical monomer and, as a consequence, to obtain polymers of an ordered structure with the "head-to-head" and "tail-to-tail" combinations prevailing [39, 103, 104]. This result was obtained on the introduction of dichloride both in solid form and in solution. The regularity of the structure of the polymers formed is the higher (and K_M the lower) the smaller the rate of supply of chloride: in the first case the time addition (dissolution) is about 0.5 min and in the second, 15 min.

Having used unsymmetrical monomers with different activities of OH groups ($6.5 < r < 22$), the authors learned that an increase in r under the conditions of a gradual introduction of the symmetrical monomer lowers K_M, i.e. favours the formation of polymers with a more ordered microstructure containing mostly the "head-to-head" ("tail-to-tail") sequences [39, 105, 106].

The order of the introduction of monomers into the reaction zone was shown to define the character of the dependence of the microstructure of polymers synthesized on the temperature of polycondensation and on the concentration of monomers [105].

A theoretical analysis carried out by Kuchanov *et al.* [39, 62] demonstrated that the values of the microheterogeneity coefficients K_M are greatly influenced by the structure and the mode of introduction of the initial compounds into the reaction sphere. Thus, the K_M values of polyesters calculated on the basis of experimental data coincide well, when plotted on the theoretical graph of the dependence of K_M on r (Fig. 5), with the K_M data determined from this theoretical dependence for the experimentally found r values of unsymmetrical diols. These findings, on the one hand, confirm

the correctness and general character of the conclusions made by Korshak *et al.* about the effect of the conditions of acceptor-catalytic polyesterification on the microstructure of the appearing macromolecules. On the other hand, the predictability of the structure of synthesized polymers on the basis of the experimental values of r is proved. The results discussed above show unequivocally that under the conditions of non-equilibrium polycondensation

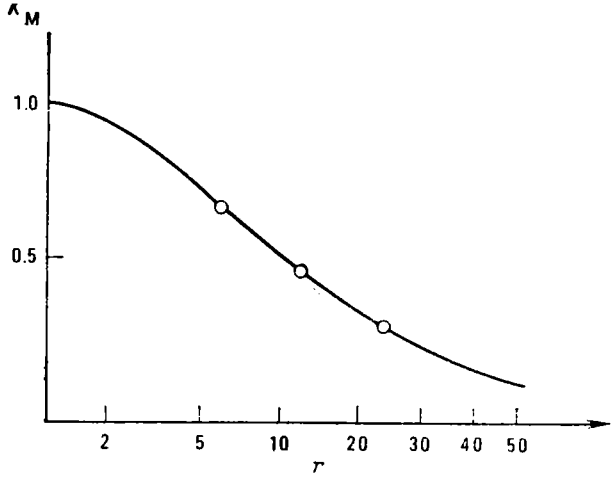


Fig. 5. The theoretical dependence of K_M of polymers on the relative activity of diol OH groups on the gradual introduction of the symmetrical monomer (○: experimental points) [105]

with the participation of unsymmetrical monomers it is possible to purposefully synthesize polymers of a predetermined microstructure and hence with a desired set of valuable properties.

Experiments conducted in the 1970s by Pino *et al.* [107-109] fully confirmed the correctness of the conclusions and generalizations made above. In 1974 the authors reported about the results of studies of the structure of polyamides and polyesters produced by interphase polycondensation of symmetrical diamines or glycols and unsymmetrical sulphide-containing dicarboxylic acids and diamines [107]. The structure of the macromolecules synthesized was determined by PMR spectroscopic analysis of their decomposition products. It was shown that the concentration of the "head-to-tail" sequence in polyesters and polyamides can range between 47 and 19 mol. % and this corresponds to the variation of their microstructure from random to restricted regular.

In subsequent experiments in 1978 Pino *et al.* [108, 109] analysed structural isomerism related to different combinations of "heads" and "tails" in the chains of polyamides prepared from ethylene

diamine and unsymmetrical dicarboxylic acid (HOOC—CH_2—S—CH_2-1,4-C_6H_4—COOH) chloride or di-*p*-nitrophenyl ester. Polycondensation was carried out either in dimethyl sulphoxide solution or at the interphase boundary. The structure of polyamides was determined by PMR.

The authors were able to show unequivocally that rapid introduction of the symmetrical monomer (ethylenediamine) into the solution of the unsymmetrical monomer (di-*p*-nitrophenyl ester of dicarboxylic acid) gives rise to polyamides with microstructure close to random (K_M=1.20). Gradual (for 5 min) addition of ethylenediamine to the solution of the unsymmetrical monomer favours the formation of polyamides with K_M=0.26, i.e. with the prevalence of the "head-to-head" ("tail-to-tail") additions.

Summarizing the results of studies of the microstructure of polycondensation polymers and the regularities of its formation, one can make the following conclusions. There is much in common between copolymers and polymers of the "head-to-tail" type. By now, the basic ways of the control of the microstructure of such polymers obtained by non-equilibrium polycondensation in a homophase system have been defined. This makes it possible to vary, by changing the reaction conditions, the structure and, accordingly, the properties of polymers in broad limits. Nevertheless, the range of variation is limited by certain boundaries related, on the one hand, to the difference in the activities of comonomers (the functional groups of the unsymmetrical monomer) and, on the other hand, to the activity of the functional groups of the intermonomer (symmetrical monomer).

One of the most general and promising approaches to the solution of the problems outlined above is the transfer from polycondensation occurring in the kinetic zone to the process defined by diffusion parameters, i.e. the change-over from a homophase system to a heterophase one. In this context, the results of studies of non-equilibrium copolycondensation in a heterophase system give reasons for optimistic forecasts.

It should also be emphasized that the task becomes more complicated if the number of monomers (e.g. unsymmetrical monomers) in the system grows. Such a picture will be observed, for instance, in going from polycondensation of a symmetrical and an unsymmetrical monomer to polycondensation of two unsymmetrical monomers.

A theoretical analysis of this and similar systems will undoubtedly outline concrete, clear directions of the development of experimental studies dealing with the synthesis of polycondensation polymers of a specified structure.

References

1. V.V. Korshak, *Raznozvennost' of Polymers*, Moscow, Nauka, 1977 (in Russian).
2. V.A. Vasnev and S.V. Vinogradova, *Usp. Khimii*, 48, No. 1, 30 (1979).
3. V.A. Vasnev, *Chemistry and Technology of High-molecular Compounds. Advances in Science and Technology Series*, Moscow, VINITI, vol. 18, 3 (1983) (in Russian).
4. F.P. Price, *J. Chem. Phys.*, 36, 209 (1962).
5. P.J. Flory, *Principles of Polymer Chemistry*, New York, Cornell Univ. Press, 1953.
6. G.A. Shtraikhman, *Zh. Prikl. Khim.*, 32, No. 3, 673 (1969).
7. K. Tyuzyo, *J. Polymer Sci., Ser. A*, 3, 3654 (1965).
8. E. Turska and M. Siniarska-Kapuscinska, *Eur. Polym. J., Suppl.*, 431 (1969).
9. E. Turska, S. Borynec, and L. Pietrzak, *J. Appl. Polym. Sci.*, 18, 667 (1974).
10. E. Turska, S. Borynec, and V. Sulkovski, *Usp. Khimii*, 48, No. 1, 51 (1979).
11. Yu.A. Fedotov, I.I. Il'in, L.B. Sokolov, Yu.A. Shapirovskii, and P.A. Chernyavskii, *Vysokomolek. Soed.*, **24B**, No. 5, 383 (1982).
12. M.S. Sandhu and R.D. Fields, *J. Polymer Sci., Chem. Ed.*, 18, 1189 (1980).
13. L.F. Beste, *J. Polymer Sci.*, 36, 313 (1959).
14. M. Lavalou, *Ann. chim. (France)* 6, 835 (1961).
15. V.Z. Nikonov, L.B. Sokolov, G.V. Babur, Yu.V. Sharikov, and E.A. Emelin, *Vysokomolek. Soed.*, **11A**, No. 4, 739 (1969).
16. L.C. Case, *J. Polymer Sci.*, 29, 455 (1958).
17. F. Lopez-Serrano, J.M. Castro, C.W. Macosko, and M. Tirrell, *Polymer*, 21, 163 (1980).
18. E. Ozizmir and G. Odian, *J. Polymer Sci., Chem. Ed.*, 18, 2281 (1980).
19. S.I. Kuchanov, and L.M. Pis'men, *Vysokomolek. Soed.*, **14A**, No. 1, 131 (1972).
20. S.I. Kuchanov and L.M. Pis'men, *Vysokomolek. Soed.*, **14A**, No. 4, 886 (1972).
21. S.I. Kuchanov, *Vysokomolek. Soed.*, **15A**, No. 9, 2140 (1973).
22. S.I. Kuchanov, *Vysokomolek. Soed.*, **16A**, No. 5, 1125 (1974).
23. J.H. Mackey, V.A. Pattison, and J.A. Pawlak, *J. Polymer Sci., Chem. Ed.*, 16, 2849 (1978).
24. S.I. Kuchanov and E.B. Brun, *Vysokomolek. Soed.*, **21A**, No. 3, 700 (1979).
25. H. Sawada, *J. Polymer Sci., Ser. B*, 1, 659 (1963).
26. H. Sawada, *J. Polymer Sci., Ser. B*, 2, 507 (1964).
27. T.M. Gritsenko, *Dokl. Akad. Nauk SSSR*, 215, No. 5, 1121 (1974).
28. T.M. Gritsenko, *J. Macromol. Sci., Ser. A*, 9, 357 (1975).
29. L.H. Peebles, *Macromolecules*, 7, 872 (1974).
30. S.I. Kuchanov, *Dokl. Akad. Nauk SSSR*, 229, No. 1, 135 (1976).
31. S.I. Kuchanov, *Vysokomolek. Soed.*, **18A**, No. 8, 1878 (1976).
32. S.I. Kuchanov, *Dokl. Akad. Nauk SSSR*, 249, No. 4, 899 (1979).
33. S.V. Korolyov, E.B. Brun, and S.I. Kuchanov, in: *Mathematical Methods in Polymer Research*, Pushchino, 1982, p. 63 (in Russian).
34. D. Durand and C.-M. Bruneau, *Makromol. Chem.*, 180, 2947 (1979).
35. D. Durand and C.-M. Bruneau, *Makromol. Chem.*, 181, 421 (1980).
36. D. Durand and C.-M. Bruneau, *Makromol. Chem.*, 181, 1673 (1980).
37. D. Durand and C.-M. Bruneau, *Eur. Polymer J.*, 17, 707 (1981).
38. D. Durand and C.-M. Bruneau, *Eur. Polymer J.*, 17, 715 (1981).
39. V.V. Korshak, S.V. Vinogradova, S.I. Kuchanov, V.A. Vasnev, G.D. Markova, and A.I. Tarasov, *Vysokomolek. Soed.*, **16A**, No. 9, 1992 (1974).
40. V.V. Korshak and S.V. Vinogradova, *Equilibrium Polycondensation*, Moscow, Nauka, 1968 (in Russian).

41. V.V. Korshak and S.V. Vinogradova, *Non-equilibrium Polycondensation*, Moscow, Nauka, 1972 (in Russian).
42. I.Ya. Slonim and Ya.G. Urman, *NMR Spectroscopy of Heterochain Polymers*, Moscow, Khimiya, 1982 (in Russian).
43. R. Yamadera and M. Murano, *J. Polymer Sci.*, A 1, 5, 2259 (1967).
44. Ya.G. Urman, I.Ya. Slonim, S.G. Alekseeva, R.S. Barshtein, and V.S. Kalinina, *Vysokomolek. Soed.*, **17A**, 1530 (1975).
45. T.S. Khramova, Ya.G. Urman, O.A. Mochalova, F.M. Medvedeva, and I.Ya. Slonim, *Vysokomolek. Soed.*, **10A**, 894 (1968).
46. Ya.G. Urman, T.S. Khramova, G.M. Avdeeva, L.N. Sedov, and I.Ya. Slonim, *Vysokomolek. Soed.*, **14A**, 2597 (1972).
47. T.S. Khramova, Ya.G. Urman, G.M. Avdeeva, L.N. Sedov, and I.Ya. Slonim, *Vysokomolek. Soed.*, **15A**, 148 (1973).
48. Ya.G. Urman, S.G. Alekseeva, and I.Ya. Slonim, *Vysokomolek. Soed.*, **19A**, 299 (1977).
49. T. Hongo, H. Suzuki, M. Murano, K. Shirasugi, and R. Yamadero, *Chem. High Polymer (Japan)*, 28, 407 (1971).
50. R. Chujo, K. Koyama, I. Ando, and I. Inoue, *Polymer J.*, 3, 394 (1972).
51. F.L. Hamb, *J. Polymer Sci., Polymer Chem. Ed.*, **10**, 3217 (1972).
52. E.E. Riecke and F.L. Hamb, *J. Polymer Sci., Polymer. Chem. Ed.*, **15**, 593 (1977).
53. Ya.S. Vygodskii, S.V. Vinogradova, Z.M. Nagiev, V.V. Korshak, Ya.G. Urman, G. Reinisch, and G. Rafler, *Acta Polymerica*, 33, 131 (1982).
54. V.V. Korshak, V.A. Vasnev, S.V. Vinogradova, P.O. Okulevich, and Yu.I. Perfilov, *Dokl. Akad. Nauk SSSR*, **204**, 1129 (1972).
55. V.V. Korshak, S.V. Vinogradova, P.O. Okulevich, Yu.I. Perfilov. V.A. Vasnev, and E.I. Fedin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 7, 1629 (1972).
56. V.A. Vasnev and S.I. Kuchanov, *Usp. Khimii*, **42**, 2194 (1973).
57. V.V. Korshak, S.V. Vinogradova, V.A. Vasnev, Yu.I. Perfilov, and P.O. Okulevich, *J. Polymer Sci., Polymer Chem. Ed.*, **11**, No. 9, 2209 (1973).
58. V.V. Korshak, V.A. Vasnev, S.V. Vinogradova, Yu.I. Perfilov, P.O. Okulevich, and G.D. Markova, *Vysokomolek. Soed.*, **16B**, 543 (1974).
59. V.V. Korshak, S.V. Vinogradova, V.A. Vasnev, Yu.I. Perfilov, and P.O. Okulevich, *Vysokomolek. Soed.*, **16A**, 2456 (1974).
60. E.A. Turska, *Vysokomolek. Soed.*, **15A**, 393 (1973).
61. S.V. Vinogradova, V.V. Korshak, P.O. Okulevich, Yu.I. Perfilov, and V.A. Vasnev, *Vysokomolek. Soed.*, **15B**, 470 (1973).
62. S.I. Kuchanov, *Methods of Kinetic Calculations in Polymer Chemistry*, Moscow, Khimiya, 1978 (in Russian).
63. P.A. Curnuck and M.E.B. Jones, *Brit. Polymer J.*, 5, 21 (1975).
64. J.H. Mackey, V.A. Pattison, and J.A. Pawlak, *J. Polymer Sci., Polymer Chem. Ed.*, **16**, 2849 (1978).
65. M. Matlengiewich, M. Gibas, and E. Turska, *J. Appl. Polymer Sci.*, **23**, 3255 (1979).
66. E.V. Gouinlock, R.A. Wolfe, and J.C. Rosenfeld, *J. Appl. Polymer Sci.*, 20, 949 (1976).
67. N. Ogata, K. Sanui, and T. Onozaki, *Kobunshi Ronbunshu*, **35**, 551 (1978).
68. N. Ogata, K. Sanui, and S. Kamiyama, *J. Polymer Sci., Polymer Chem. Ed.*, **16**, 1991 (1978).
69. I.M. Raigorodskii, Ya.G. Urman, E.Sh. Gol'berg, S.G. Alekseeva, V.A. Savin, and I.Ya. Slonim, *Vysokomolek. Soed.*, **20A**, 1486 (1978).
70. V.V. Korshak, I.Ya. Slonim, S.V. Vinogradova, Ya.G. Urman, V.A. Vasnev, A.Kh. Bulai, and T.M. Gogiashvili, *Vysokomolek. Soed.*, **22B**, 4 (1980).
71. V.A. Vasnev, T.M. Gogiashvili, B.D. Lavrukhin, S.V. Vinogradova, and V.V. Korshak, *Vysokomolek. Soed.*, **23A**, 2537 (1981).

72. V.V. Korshak, V.A. Vasnev, S.V. Vinogradova, T.M. Gogiashvili, I.Ya. Slonim, Ya.G. Urman, A.Kh. Bulai, and R.G. Keshelava, *Vysokomolek. Soed.*, **23A**, 2567 (1981).
73. V.V. Korshak, S.V. Vinogradova, V.A. Vasnev, T.M. Gogiashvili, I.Ya. Slonim, Ya.G. Urman, and A.Kh. Bulai, *Vysokomolek. Soed.*, **24A**, 325 (1982).
74. V.V. Korshak, S.V. Vinogradova, V.A. Vasnev, G.D. Markova, and T.V. Lecae, *J. Polymer Sci., Polymer Chem. Ed.*, **13**, 2741 (1975).
75. E. Izard, *J. Polymer Sci.*, 8, 503 (1952).
76. K. Doak and H. Campbell, *J. Polymer Sci.*, **18**, 215 (1955).
77. Zh.S. Sogomonyants and M.V. Vol'kenshtein, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 5, 611 (1957).
78. G.N. Chelnokova and V.V. Korshak, *On High-molecular Compounds*, Collected articles on general chemistry, ed. by A.E. Arbuzov *et. al.*, Moscow, Leningrad, USSR Academy of Sciences, 1953, vol. 2, 1070.
79. G.N. Chelnokova, V.V. Korshak, and S.R. Rafikov. *On High-molecular Weight Compounds*, Collected articles on general chemistry, ed. by A.E. Arbuzov *et. al.*, Moscow, Leningrad, USSR Academy of Sciences, 1953, vol. 2, 1075 (in Russian).
80. V.V. Korshak, G.N. Chelnokova, and G.I. Distler, *On High-molecular Compounds*, Collected articles on general chemistry, ed. by A.E. Arbuzov *et al.*, Moscow, Leningrad, USSR Academy of Sciences, 1953, vol. 2, 1278 (in Russian).
81. I. Panaiotov, *Compt. Rend. Acad. Bulgare Sci.*, **16**, 39 (1963).
82. J. Preston and R. Smith, *J. Polymer Sci., Polymer Letters*, **B4**, 1033 (1966).
83. J. Preston, *J. Polymer Sci., Polymer Chem. Ed., A-1*, 4, 529 (1966).
84. B. Culbertson and R. Murphy, *J. Polymer Sci., Polymer* Letters, **B4**, 249 (1966).
85. B. Culbertson and R. Murphy, *J. Polymer Sci., Polymer Letters*, **B5**, 807 (1967).
86. E.S. Krongauz, V.V. Korshak, and A.L. Rusanov, *Dokl. Akad. Nauk SSSR*, **180**, 1105 (1968).
87. G. Roques and J. Neel, *Bull. Soc. Chim. France*, No. 9, 3377 (1967).
88. R. Salle, B. Sillion, and G. Gaudemaris, *Compt. rend. Acad. sci. France*, **C267**, 1213 (1968).
89. J. Preston, W. De Winter, W. Black, and W. Hofferbert, *J. Polymer Sci., Polymer Chem. Ed., A-1*, 7, 3027 (1969).
90. J. Preston, *J. Polymer Sci., Polymer Chem. Ed., A-1*, 8, 3135 (1970).
91. J. Preston, *J. Polymer Sci., Polymer Chem. Ed., A-1*, **10**, 3373 (1973).
92. J. Preston, W. Black, and W. Hofferbert, *J. Macromol. Sci., Chem.*, **7A** 67, (1973).
93. R. Morrison, J. Preston, J. Randall, and W. Black, *J. Macromol. Sci., Chem.*, **7A**, 99 (1973).
94. J. Randall, R. Morrison, and J. Preston, *J. Macromol. Sci., Chem.*, **7A**, 119 (1973).
95. J. Preston and H. Morgan, *J. Macromol. Sci., Chem.*, **7A**, 325 (1973).
96. C. Giori, *J. Amer. Chem. Soc. Polymer Prepr.*, **11**, 326 (1970).
97. C. Giori, *J. Amer. Chem. Soc. Polymer Prepr.*, 12, 606 (1971).
98. N. Okata and T. Ikari, *J. Polymer Sci., Polymer Chem. Ed.*, **11**, 1939 (1973).
99. Y. Imai and N. Okunoyama, *J. Polymer Sci., Polymer Chem. Ed., A-1*, **10**, 2257 (1972).
100. N. Kobayashi and T. Fujisawa, *Macromolecules*, 5, 1106 (1972).
101. N. Kobayashi and T. Fujisawa, *J. Polymer Sci., Polymer Chem. Ed., A-1*, **10**, 1233 (1972).
102. N. Kobayashi, A. Osawa, and T. Fujisawa, *J. Polymer Sci., Polymer Letters*, **10B**, 515 (1972).
103. V.V. Korshak, S.V. Vinogradova, V.A. Vasnev, G.D. Markova, and T.V. Lecae, *J. Polymer Sci., Polymer Chem. Ed.*, **13**, 2741 (1975).

104. I.Ya. Slonim, V.A. Vasnev, A.Kh. Bulai, Ya.G. Urman, G.D. Markova, V.V. Korshak, and S.V. Vinogradova, *Vysokomolek. Soed.*,'22A, 2792 (1980).
105. Z. Jedlinski, D. Sek, U. Gaic, G.D. Marcova, V.A. Vasnjov, S.V. Vinogradova, and V.V. Korshak, *Acta polymerica*, **B31**, 100 (1978).
106. V.V.Korshak, G.D. Markova, I.L. Slonim, V.A. Vasnev, S.V. Vinogradova, Ya.G. Urman, and A.Kh. Bulai, *Vysokomolek. Soed.*, **24A**, 1270 (1982).
107. P. Pino, P. Casartelli, J. Guiroga, and G. Lorenzi, *Prepr. International Symposium on Macromolecules.* IUPAC. Madrid, Sept., 15-20, 1974, v. 1, p. 255.
108. P. Pino, G. Lorenzi, G. Casartelli, A. Steinmann, F. Bonner, and J. Guiroga, *Macromolecules*, **11**, 624 (1978).
109. P. Pino, G. Lorenzi, U. Suter, P. Casartelli, and A. Steinmann, *Amer. Chem. Soc. Polym. Prepr.*, **19**, 267 (1978).

5 Thermostable Heterocyclic Polymers

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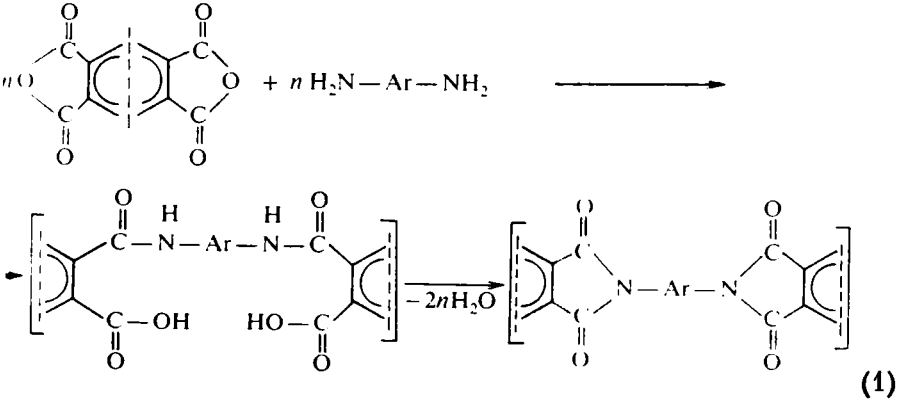
1. INTRODUCTION

The last 25 years have witnessed in the world's industrialized nations a considerable increase in research designed to develop thermostable polymers and materials based thereon [1-4]. An impetus to the studies has been provided by the growing demand for these materials in rapidly developing industrial applications such as aircraft, special mechanical parts, electronics, etc. Among the potential routes towards thermostable polymers, the synthesis of aromatic heterocyclic polymers, polyheteroarylenes, achieved the most progress. Advances in the chemistry of polyheteroarylenes resulted in the elaboration of a great number of thermostable heterocyclic polymers, the majority of which could be subdivided into several basic classes.

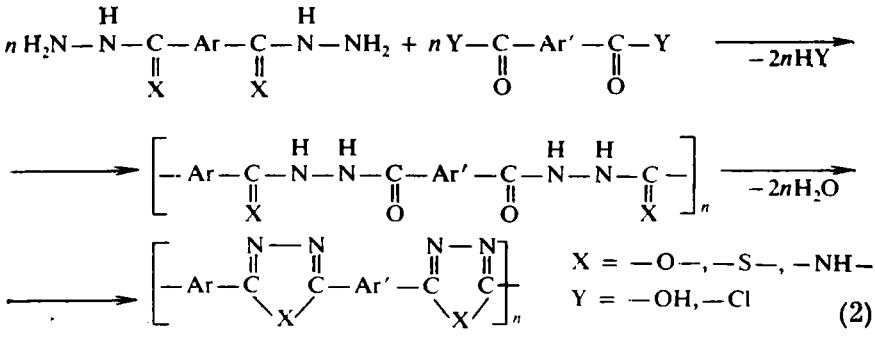
Aromatic polyimides [5-9], which are products of reaction between aromatic diamines and bis(phthalic anhydrides) according to the general scheme



(1)

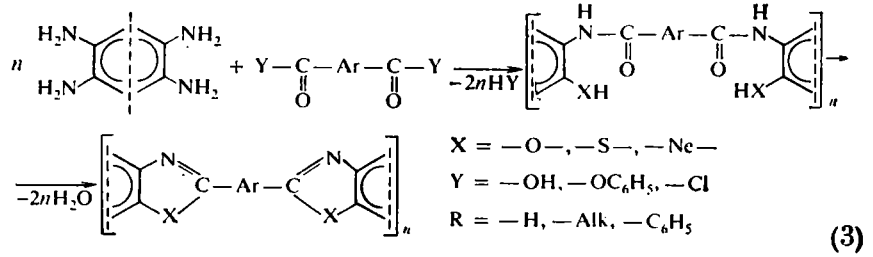
became the most common among the polyheteroarylenes and outstepped the limits of laboratory studies.

Fewer possible applications could be visualized for aromatic polyazoles [9-12] synthesized according to the scheme



(2)

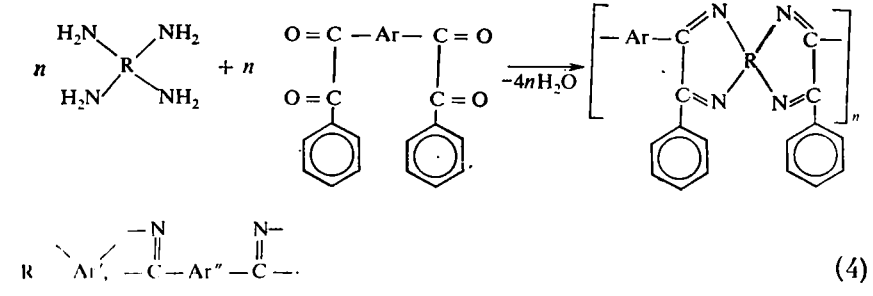
Only poly-1,3,4-oxadiazoles [X=—O— in Eq. (2)] can be considered promising systems not only from the scientific, but also from the practical point of view. Among the aromatic polybenzazoles prepared by reacting *o*, *o'*-disubstituted aromatic diamines with dicarboxylic acids or their derivatives [9-12]:



(3)

a larger use has been found in polybenzoxazoles [X=—O— in Eq. (3)] and polybenzimidazoles [X=—NH— in Eq. (3)].

Polyphenylquinoxalines [13, 15, 16] [R= Ar' in Eq. (4)] are perhaps the most attractive aromatic polybenzazines, which are reaction products of bis-α-dicarbonyl compounds [13] with bis(*o*-phenylenediamines) and bisamidrazones [14]:



(4)

Products based on these polyheteroarylenes are stably serviceable at temperatures of 250 to 300 °C and exhibit a valuable set of properties. Some of the polyheteroarylenes of the above classes are being produced or are on the verge of commercial or semi-commercial production [17].

The chemistry and technology of each of the above mentioned conventional classes of polyheteroarylenes have been largely promoted by Soviet scientists who, along with their foreign counterparts, furnished a lot of new information about the polyimides (Institute of High-molecular Compounds of the USSR Academy of Sciences, Karpov Institute of Physical Chemistry, Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences, Institute of Chemical Sciences of the Kazakh Academy of Sciences, Research and Production Enterprises "Plastmassy" and "Khimvolokno"), the polyazoles (Institute of Organoelement Compounds of the USSR Academy of Sciences, Research and Production Enterprises "Plastmassy" and "Khimvolokno"), polybenzazoles (Mendeleev Moscow Institute of Chemical Technology, Karpov Institute of Physical Chemistry, Nesmeyanov Institute of Organoelement Compounds of the USSR Academy of Sciences, Research and Production Enterprise "Plastmassy"), and polyphenylquinoxalines (Institute of Organoelement Compounds of the USSR Academy of Sciences, Research and Production Enterprise "Plastmassy").

In the course of the recent 15 years, Soviet scientists have vigorously addressed themselves to research into the possibility of deliberately modifying the properties of polyheteroarylenes, as well as of the improvement of methods and techniques for the synthesis of these polymers. These studies have been stimulated by the fact that the majority of heterocyclic polymers have a number of disadvantages. Firstly, most of the above polyheteroarylenes are produced by a stepwise method which involves the reaction of the starting compounds under mild conditions, the production and separation of prepolymers, their processing into articles followed by cyclization of products obtained. Since the cyclization processes involve the separation of low-molecular by-products, particularly water, the resulting aim materials are porous, which, naturally, adversely affects their performances. And, secondly, not infrequently the solid-state cyclization of prepolymers does not afford 100% conversion [18], which increases the "raznozvennost'" (chemical heterogeneity) of polyheteroarylenes [19, 20] with respective decline of their performances. Thirdly, many prepolymers, for instance, poly[(*o*-carboxy)amides] formed by mild reaction of bis(phthalic anhydrides) with aromatic diamines [formula (1)] are unstable and inconvenient at storage and handling. In addition, most of the polyheteroarylenes in their final state are insoluble in organic solvent and this hinders their processing into articles and reuse. Moreover,

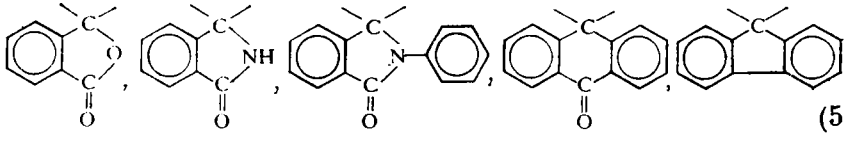
individual classes of polyheteroarylenes have specific drawbacks: the polyimides are susceptible to alkaline hydrolysis [5-9], the polybenzimidazoles do not resist thermal oxidative degradation [10-12], whereas the polyphenylquinoxalines are characterized by relatively low softening temperatures [13, 15, 16].

Finally, scarcely available, high-cost monomers, often not very stable to oxidation and hydrolysis [21], are used in the synthesis of polyheteroarylenes, providing additional obstacles to the development of the chemistry and technology of these polymers.

The efforts of Soviet investigators were primarily aimed at imparting the solubility in organic solvents to polyheteroarylenes, at enhancing their thermostability, as well as at providing new methods for the synthesis of these systems having substantial advantages over the known processes.

2. POLYHETEROARYLENES SOLUBLE IN ORGANIC SOLVENTS

The most significant and essential contribution of Soviet investigators into the chemistry of polyheteroarylenes soluble in organic solvents is probably the development of the so-called "cardo" polyheteroarylenes [22-24]. The "cardo", or "loop-like", structure of the polymer derives from the use, in the polycondensation process, of at least one monomer containing a carbon atom which enters both the main chain of the aim macromolecule and the bulky side grouping. Typical of "cardo" groupings is a system of the type



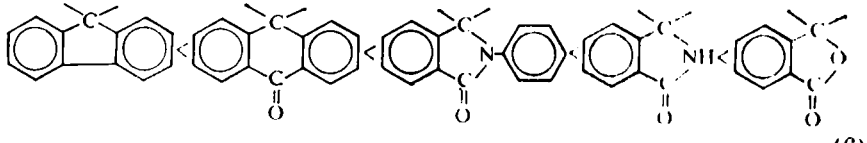
(5)

widely used to impart solubility to poly-1,3,4-oxadiazoles [25-30], polyimides [32-39], and other polyheteroarylenes [24].

Regarding the family of "cardo" poly-1,3,4-oxadiazoles, the most thorough study has been dedicated to the systems based on 3,3′-bis(4-carboxyphenyl)phthalide and its derivatives, acid dichloride and dihydrazide. Two methods have been envisaged for the preparation of these polymers, a two-stage process according to the reaction scheme (2), and a single-stage high-temperature polyheterocyclization in polyphosphoric acid (PPA) [28, 31]. The latter proved to be preferable and was used for the preparation of various poly-1,3,4-oxadiazoles, characterized by combination of high molecular masses, solubility in organic solvents, and heat and thermal stability.

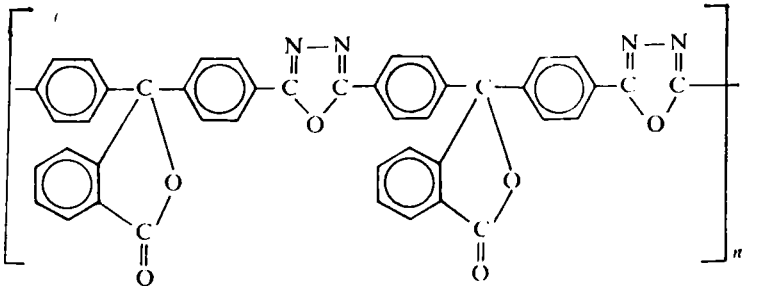
"Cardo" polyimides received still more attention [32-39]. Like the above discussed polyimides, they can be produced by a two-stage method [32] accomplished according to scheme (1). On the other hand, these polymers can be obtained via a single-stage high-temperature polycyclization in organic solvents such as nitrobenzene, benzonitrile, sulpholane, α-chloronaphthalene, and cresol [34, 35]. According to this method of the synthesis, which looks more attractive than the two-stage one, the reactions of cyclization and macromolecule propagation proceed in parallel; moreover, the limiting step of the process is formation of (*o*-carboxy)amide fragments [36]. The single-stage high-temperature synthesis of polyimides has been widely used to obtain desired forms of polyimides of largely varying structures and properties [37, 38]. "Cardo" polyimides can also be obtained by catalytic imidization of poly(*o*-carboxy)amides in reaction solutions [39], using equimolar mixtures of tertiary or heterocyclic amines with acid anhydrides, particularly, a mixture of pyridine with acetic anhydride as catalysts [5-8]. This method of imidization makes it possible not only to achieve a high degree of cyclization, but also to obtain polyimides with much higher solubility in organic solvents than the same systems derived from solid-state polycyclodehydration of poly(*o*-carboxy)amides.

The favourable effect of "cardo" groupings on polyheteroarylene solubility is decreasing in the range



(6)

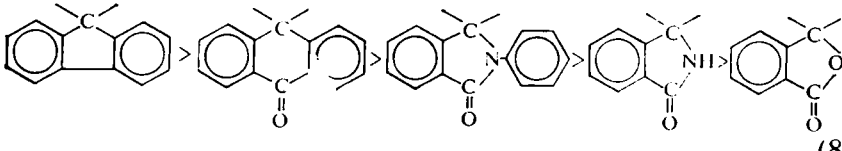
which is connected with the size, polarity, and symmetry of "cardo" groupings [24]. Consequently, poly-2,5-(4′4″-diphenylenephthalide)-1,3,4-oxadiazole



(7)

exhibits the highest solubility among the poly-1,3,4-oxadiazoles. This polymer is soluble in methylene chloride, symtetrachloroethane, dimethylformamide (DMF), dimethylacetamide (DMAA), N-methyl-2-pyrrolidone (N-MP), pyridine, benzyl alcohol, and other solvents. Quite similarly, systems containing two phthalide or phthalimide groups in each elementary unit are the best soluble among the "cardo" polyimides [24].

An outstanding feature of "cardo" substituents is that, unlike phenyl substituents, commonly used to enhance the solubility of polyheteroarylenes [40], they do not diminish the heat resistance of polymers: practically all of the "cardo" polyheteroarylenes are characterized by high second - order glass-transition (softening) temperatures [22-24]. The role of "cardo" groupings in the heat stability of polyheteroarylenes is different, and, according to Ref. [41], determined by the ratio of "reduced" volume of a cyclic grouping to its molecular weight, K_v/M. In general, the decrease of heat stability of polyheteroarylenes as a function of "cardo" grouping type, found out for polyarylates [41]



(8)

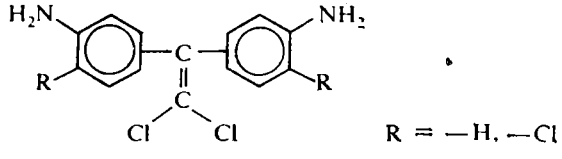
looks true for polyheteroarylenes as well.

"Cardo" polyheteroarylenes exhibit high thermostability [33, 34], largely depending on the nature of "cardo" groups; systems containing fluorene and anthrone groupings [34] are characterized by the highest thermostability.

On the whole, the "cardo" polymers are not inferior to conventional polyheteroarylenes with respect to thermal and heat stability, or even surpass them. These polymers should be more conveniently processed from solutions into films, fibres, varnish coatings, etc. [22-24].

It will, however, be pointed out that the synthesis of "cardo" polyheteroarylenes is often associated with the use of not readily available and costly monomers [21], which substantially hampers the development of this particular field of polymer chemistry and technology. Consequently, the problem of providing a reliable source of starting materials for these polymers looks very urgent. Of significant interest in this respect are some derivatives of DDT [42], a widespread and commercially produced insecticide, which has lost its practical value, and specifically some DDT-based di-

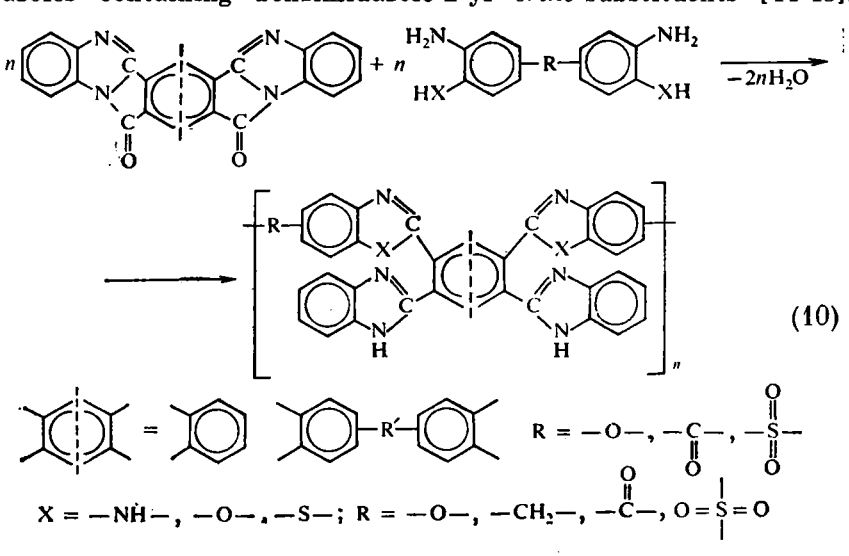
amines containing 1,1-dichloroethylene groupings:



(9)

which represent a species of "cardo" groups. A number of polyimides soluble in organic solvents and having elevated fire resistance [43] have been produced from these diamines.

Along with "cardo" polyheteroarylenes, the Soviet scientists developed soluble heterocyclic polymers containing heterocyclic substituents and having a thermal stability not lower than that of the fragments of the base macromolecular chains. In particular, the reaction of bis(1,2-benzoylenebenzimidazoles) with tetrafunctional nucleophilic compounds under the conditions of high-temperature polycyclocondensation in PPA or *m*-cresol yielded polybenzazoles containing benzimidazole-2-yl *ortho*-substituents [44-48]:



(10)

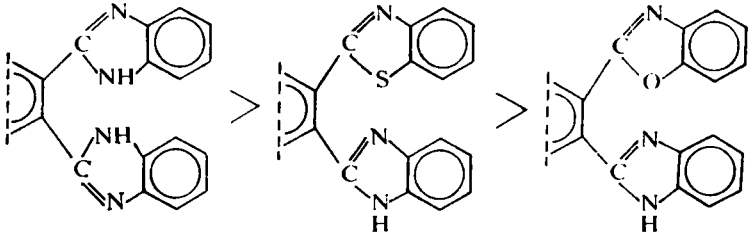
Scheme (10) is analogous to the reaction scheme (3) except that the acidic reaction components are unusual "latent" dicarboxylic acids, bis(1,2-benzoylenebenzimidazoles). The polybenzazoles thus obtained which contain benzimidazol-2-yl *o*-substituents are characterized by a significantly better solubility than their unsubstituted analogues. The systems containing no "hinged" groups are soluble in formic and trifluoroacetic acids, as well as in hot hexamethylphosphamide (HMPA). Introduction of "hinged" groups

into benzimidazolyl-substituted polybenzazoles makes them soluble in DMF, DMAA, N-MP, dimethylsulphoxide (DMSO), *m*-cresol, and a mixture of tetrachloroethane (TCE) with phenol (3 : 1).

Practically all the polymers have high viscosity characteristics corresponding to weight-average molecular masses from 50 000 to 300 000.

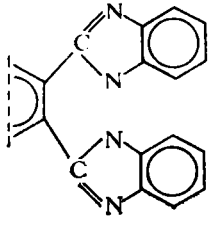
The incorporation of benzimidazol-2-yl *ortho*-substituents provides different effects on the heat stability of polybenzimidazoles, polybenzoxazoles, and polybenzthiazoles; introduction of substituents almost does not alterate the softening temperatures of polybenzimidazoles, but substantially increases the softening temperatures of polybenzoxazoles and polybenzthiazoles.

The thermal stability of poly[(benzimidazol-2-yl)benzazoles] under conditions of dynamic TGA is comparable with that of their unsubstituted analogues. The thermal oxidative stability of various poly[(benzimidazole-2-yl)benzazoles] under isothermal conditions at 400 °C revealed that this property decreases through the range:



(11)

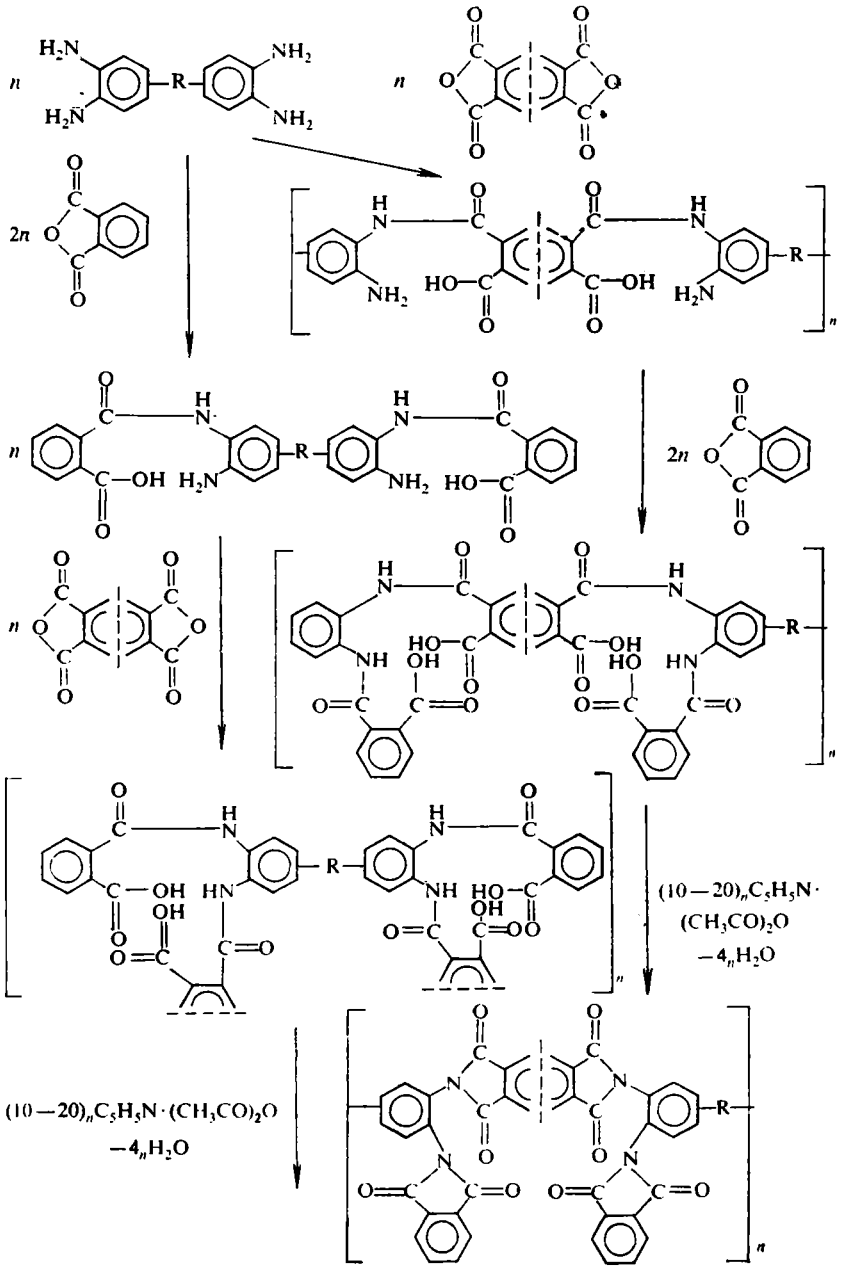
Superior thermal oxidative stability of polybenzimidazoles as compared with other polybenzazoles, which is not characteristic of unsubstituted systems of this type [1, 2] could be attributed to intramolecular dehydration occurring at high temperatures with formation of condensed structures of the type



(12)

as well as to the eventual intermolecular dehydration reactions and formation of "cross-linked" structures.

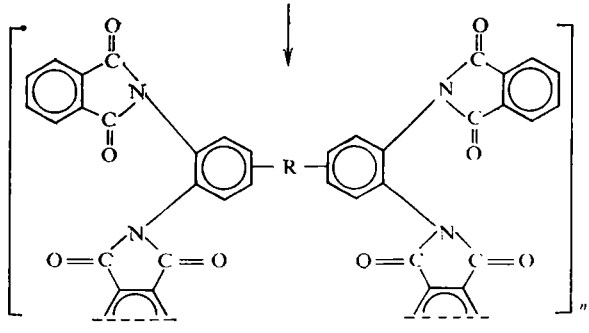
High thermal properties, good solubility in organic solvents, and high molecular masses make the poly[(benzimidazol-2-yl)benzazoles] promising systems for the production of various heat-,

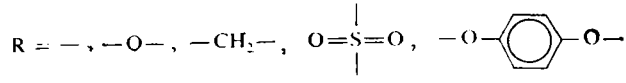


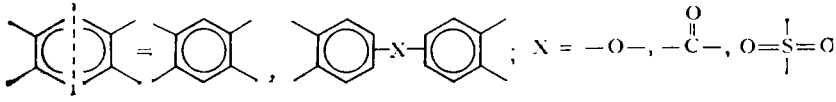
(13)

thermo-, and chemically resistant materials with superior mechanical properties.

Another approach to the synthesis of heteryl-substituted polyheteroarylenes involves the preparation of polyimides containing arimide *ortho*-substituents [49, 50]. The synthesis of polyimides containing N-phthalimide *ortho*-substituents has been effected by treating bis(*o*-phenylenediamines) of various structures with equimolar quantities of bis(phthalic anhydrides) and two-fold quantities of phthalic anhydride added at various order, followed by chemical cyclization of poly[(*o*-carboxy)amides] containing (*o*-carboxy)amide *ortho*-substituents:







Depending on the donor-acceptor nature of groups R in the starting bis(*o*-phenylenediamines) and the order of adding phthalic and bis(phthalic) anhydrides, polymers with various ratios of *m*- to *p*-substituted fragments in the main polyimide chains are formed, thus making it possible to modify deliberately the solubility and heat stability of the aim polymers.

Synthesized polyimides are readily soluble in N-MP, DMF, DMAA, DMSO, a TCE/phenol mixture (3 : 1), *m*-cresol, etc., forming highly (up to 40%) concentrated solutions. Average-weight molecular masses of these systems vary within 25 000 to 130 000.

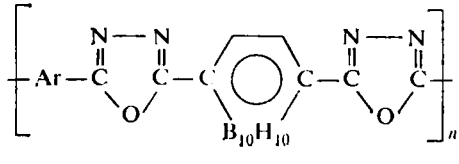
Softening temperatures of poly(*o*-phthalimido)imides are somewhat lower than those of their unsubstituted analogues [1, 2], probably due to isomeric raznozvennost' of these polymers [50].

A major research effort of Soviet scientists regarding polyheteroarylenes soluble in organic solvents has gone into organoelement

polymers. The most sizeable investigations into the organoelement polyheteroarylenes relate to the synthesis of boron-containing, especially carborane-containing systems [51, 52]. Thus, *m*- and *p*-carborane-containing polypyromellitimides have been produced by reaction of *m*- and *p*-diaminocarborane with pyromellitic dianhydride under conditions of low-temperature polycondensation followed by thermal or chemical cyclization of the poly(*o*-carboxy)amides thus obtained [53] according to a scheme analogous to the scheme represented by Eq. (1). The study of the processes of formation of carborane-containing polyimides demonstrated that in the course of cyclization, *m*-carborane fragments are transformed into dicarbondecaborate fragments, while *p*-carborane fragments undergo no destruction. The polyimides obtained in this manner were soluble in amide solvents and exhibited a specific behaviour on heating. For instance, the polyimides containing *m*-carborane fragments were undergoing oxidation in air at 250 °C without softening, while *p*-carborane-containing systems were softening at 400 - 450 °C with degradation. Yet, the incorporation of *m*-carborane fragments into polyimide macromolecules ensures greater reduction of the rate of homolytic and heterolytic degradation of imide cycles than *m*-carborane groupings [54].

Carborane-containing polyimides of other structure have been prepared from tetracarboxylic acid dianhydrides having *m*- and *o*-carborane groupings, and aromatic diamines [55, 56]. Pyrolysis of these polyimides at 1000 °C in an inert medium and in air demonstrated that diphenyl-*o*-, or diphenyl-*m*-carborane fragments with adjoining imide cycles are the most susceptible to homolytic degradation [57].

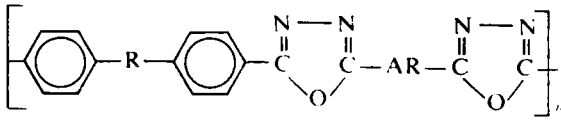
The synthesis of carborane-containing poly-1,3,4-oxadiazoles was effected according to the scheme represented by formula (2) via the preparation of carborane-containing polyhydrazides followed by their polycyclodehydration [58, 59]. Carborane-containing polyhydrazides have been obtained from *m*- and *p*-carborane dicarboxylic acid dichlorides and dicarboxylic acid dihydrazides in the presence of pyridine, or of a mixture of pyridine and tetrahydrofuran [58, 59]. The *p*-carborane-containing polyhydrazides heated under vacuum at 250-300 °C or in PPA at 140 °C yielded the corresponding poly-1,3,4-oxadiazoles; *m*-carborane-containing polyhydrazides, under the same conditions, underwent the cleavage of *m*-carborane rings caused by the interaction of the latter with hydrazide units [58, 59]. Aromatic *m*-carborane-containing poly-1,3,4-oxadiazoles of the general formula



(14)

are softening within 250-400 °C without weight loss on heating in air or in an inert medium up to 380-450 °C [58, 59].

Carborane-containing poly-1,3,4-oxadiazoles of the general formula

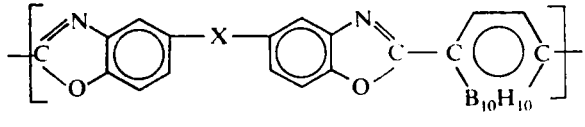


(15)

R = $-C(B_{10}H_{10})-C(O)-$, $-CB_{10}H_{10}C-$

were obtained by the reaction of 1,2- or 1,7-bis(4-carboxyphenyl)carborane acid dichlorides or dihydrazides with dihydrazides (as well as hydrazine salts) or, respectively, with other aromatic dicarboxylic acid dichlorides in PPA at 140-160 °C [60]. These polymers are softening at 260-350 °C, are readily soluble in a TCE/phenol (3 : 1) mixture forming strong elastic films.

Carborane-containing polybenzoxazoles have been obtained according to scheme (3), i.e. by the reaction of bis(*o*-aminophenols) with dicarboxylic acid dichlorides followed by thermal or chemical (in PPA) cyclocondensation of corresponding poly(*o*-hydroxy)amides [61, 62]. *m*-Carborane dicarboxylic acid dichloride has been used as a carborane-containing comonomer. The polybenzoxazoles based on this comonomer, having the general formula

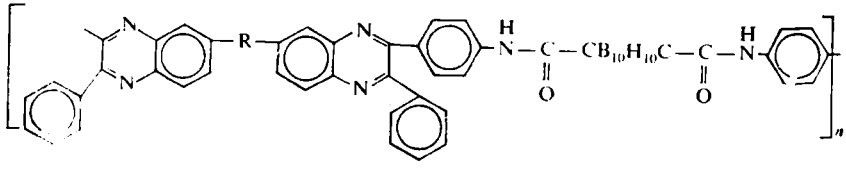


(16)

X = $-CH_2-$, $-O-$, $-C(CH_3)_2-$, $-SO_2-$

are soluble in amide solvents and in TCE/phenol (3 : 1) mixture.

Carborane-containing polyphenylquinoxalines have been obtained following scheme (4) by the reaction of bis(*o*-phenylenediamines) with *m*-carborane-containing bis(α-diketone) in *m*-cresol or in chlorinated hydrocarbons with addition of proton donors [63]. The resulting *m*-carborane-containing polyphenylquinoxalines of the general formula



R , O

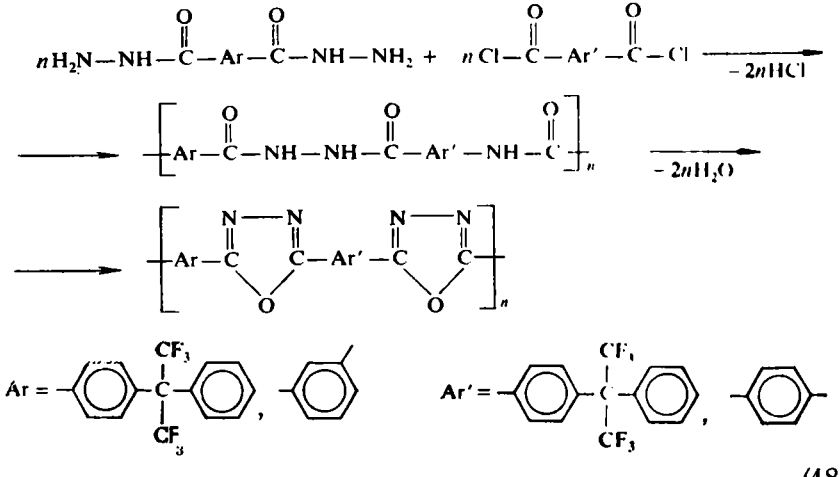
(17)

are soluble in chloroform and tetrahydrofuran; they possess good viscosity properties and begin to soften at temperatures above 280 °C. Coke residue at 800 °C is 32-57% in air, and 70-80% in an inert medium. According to Ref. [63], the *m*-carborane-containing polyphenylquinoxalines can be useful in heat- and thermostable films, coatings, adhesives, fibres, etc.

Along with carborane-containing polyheteroarylenes, considerable attention of Soviet scientists has been given to fluorinated polyheteroarylenes [64, 65] and, especially, to the systems containing hexafluoroisopropylidene groups.

Attempts of synthesizing polyimides based on pyromellitic dianhydride and 2,2-bis(4-aminophenyl)hexafluoropropane [66] by a two-stage method [scheme (1)] failed to produce soluble polyimides. Later studies [67], however, convincingly demonstrated the favourable effect of hexafluoroisopropylidene groups, introduced via amine and anhydride components, on the solubility of homo- and copolyimides in organic solvents.

Hexafluoroisopropylidene-containing poly-1,3,4-oxadiazoles have been obtained according to scheme (2), by the reaction of 2,2-bis(*p*-carboxyphenyl)hexafluoropropane dihydrazide and/or acid dichloride with the corresponding iso- and terephthalic acid derivatives, followed by thermal cyclization of the resulting polyhydrazides [66]:



(18)

A comparison of the characteristics of such poly-1,3,4-oxadiazoles proves that there is a significant (about 50 °C) decrease in softening temperatures of polyoxadiazoles passing from a structure free from hexafluoroisopropylidene groups to a structure containing a maximum amount of the latter.

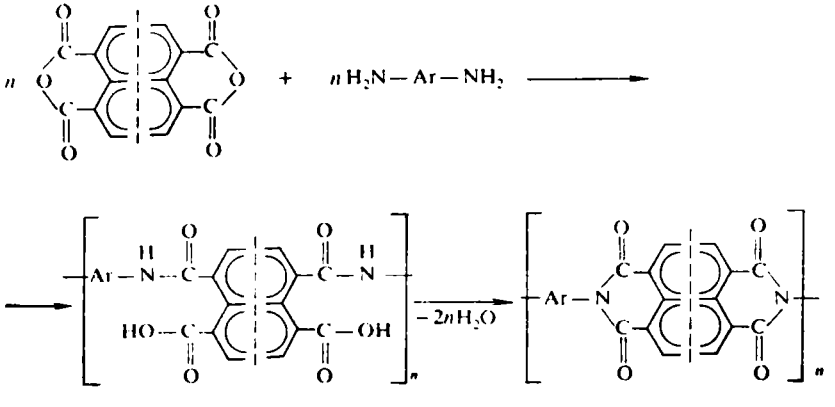
At the same time, the solubility of poly-1,3,4-oxadiazoles always increases with the proportion of fluorine atoms in the polymer and reaches the maximum in a polymer based on 2,2-bis(*p*-carboxyphenyl)hexafluoropropane acid dichloride and its hydrazide [66]; this poly-1,3,4-oxadiazole is soluble in DMF, DMSO, nitrobenzene, and a TCE/phenol mixture. The tendency of fluorinated polymers to be dissolved might be based, according to Ref. [66], on both the affinity of trifluoromethyl groups to polar solvents, and the loose structure of these polymers due to the presence of bulky substituents facilitating diffusion of the solvent.

3. POLYHETEROARYLENES WITH ENHANCED THERMAL PROPERTIES

The trend towards the synthesis of polyheteroarylenes with enhanced thermal properties followed by Soviet scientists involves the development of systems containing highly condensed heterocyclic fragments which predetermine a partially "ladder" structure of the polymers.

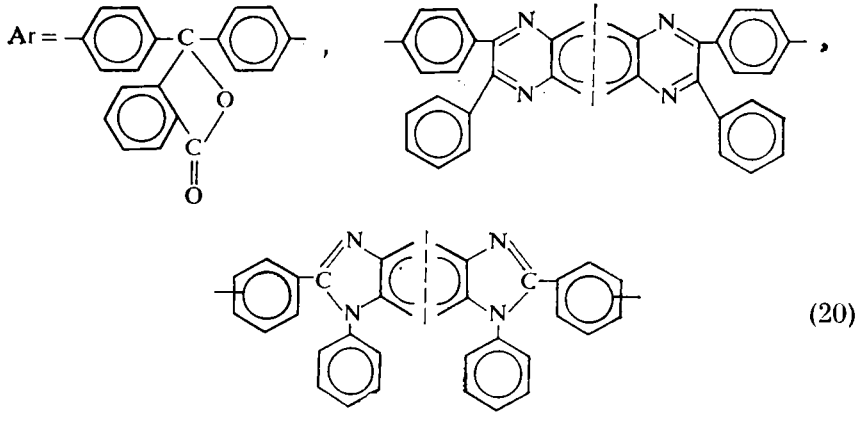
Detailed studies on model compounds and polymers [68, 69] showed that despite some formalism of the concept asserting elevated resistance of all the "ladder" systems to various kinds of degradation [70, 71], the "ladder" polymers having no weak bonds and characterized by high degrees of cyclization are in fact more thermostable than common polyheteroarylenes.

One of the most significant achievements of Soviet investigators in partially "ladder" polyheteroarylenes is the preparation of high molecular weight polynaphthylimides which could be processed into articles [72]. The synthesis of these systems is realized according to the scheme



(19)

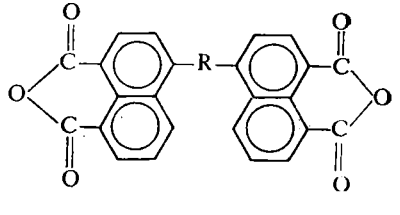
which is quite identical to that for the synthesis of polyphthalimides (see Eq. (1)), but has some specific features. Bis(naphthalic anhydrides) used as acid comonomers are characterized by a lower electrophilic reactivity as compared with bis(phthalic anhydrides) [68]; at the same time, the naphthylimide cycles are being formed under very mild conditions, due to a thermodynamic advantage of the formation of six-membered imide cycles. As a consequence, the intermediate *peri*-carboxynaphthylamide structure is practically unrecoverable, and undergoes fast cyclodehydration into the aim naphthalimide system. In order to impart solubility in organic solvents to the aim polynaphthylimides based on the most common bis(naphthalic anhydride), a naphthalene-1,4,5,8-tetracarboxylic acid derivative, aromatic diamines containing "cardo" [73, 74] or phenyl-substituted heterocyclic groupings [75, 76]



(20)

are used as amine reaction components. The synthesis of polynaphthylimides based on these comonomers is effected under conditions of high-temperature (160-200 °C) polycondensation in nitrobenzene or in phenolic solvents with carboxylic acids as catalysts, and yields high-molecular products soluble in a number of amide, phenolic, and acidic solvents [73-76].

An alternative approach to selecting monomers for the synthesis of soluble polynaphthylimides is based on the use of various bis(naphthalic anhydrides) containing "hinged" groupings as acidic reaction components [77]:



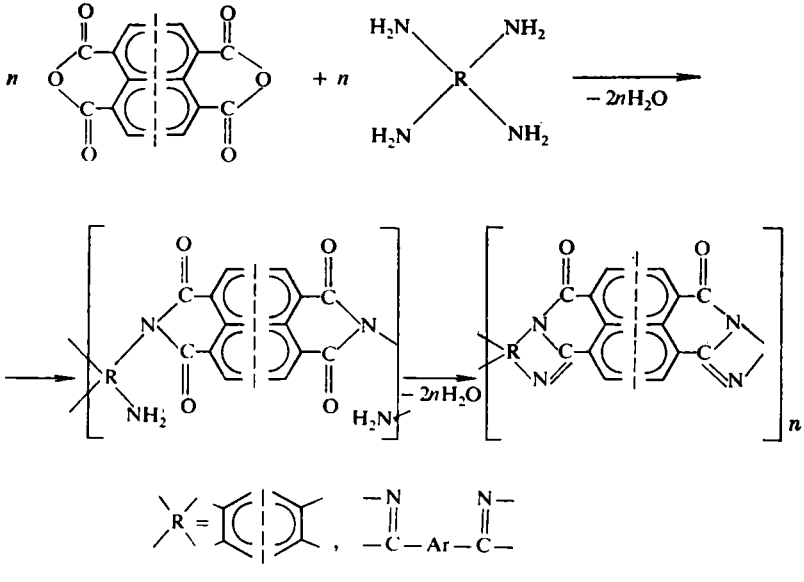
(21)

These bis(naphthalic anhydrides) are produced from a readily available acenaphthene [78] or its simplest derivatives.

The reactions of these bis(naphthalic anhydrides) with widely used aromatic diamines, such as 4,4′-diaminodiphenyloxide, 4,4′-diaminodiphenylmethane, and the like, yield high-molecular polynaphthylimides soluble in phenolic and acidic solvents [72].

Polynaphthylimides possess higher thermostability than the polyphthalimides of the corresponding structure [72]. Still more obvious is the advantage of polynaphthylimides over polyphthalimides as far as the resistance of these systems to alkaline hydrolysis is concerned. The above-discussed distinctions could be explained not only by higher resistance of the naphthylimide cycle, as compared with the phthalimide cycle, to various degradation processes, but by a lower raznozvennost' (different-unit structure) [19, 20] of polynaphthylimides as well.

These same factors determine elevated stability to thermal and hydrolytic degradation of polynaphthoyleneazoles which are products of intramolecular polycyclodehydration of poly(*o*-aminophenyl)naphthylimides [78-81]. These systems produced according to the scheme



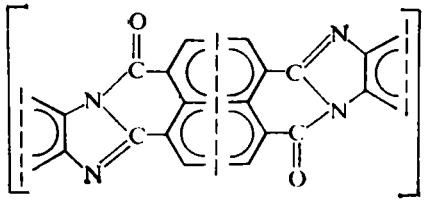
(22)

are considered as "ladder" polyheteroarylenes, prepared by a three-stage method [68, 79]. The majority of the systems, obtained by high-temperature polycyclocondensation in PPA [31, 77, 79-81], are

characterized by high molecular masses and degrees of cyclization, and are readily soluble in acids (sulphuric, methylsulphuric, PPA, etc.). Recent investigations demonstrated that high-molecular polynaphthoyleneazoles with a high degree of cyclization could be obtained under relatively mild conditions, for instance, by polycyclocondensation in phenolic solvents at 160-180 °C [82]. Moreover, when bis(*o*-phenylenediamine) and bisamidrazone containing hexafluoroisopropylidene groups are used as comonomers of naphthalene-1,4,5,8,-tetracarboxylic acid dianhydride, systems soluble in phenolic solvents [83, 84] are obtained. This opens new possibilities of processing these polymers.

Another route to soluble polynaphthoyleneazoles is the use of bis(naphthalic anhydrides), containing "hinged" groups similar to those used in Ref. [77], as acidic reaction components.

Among polynaphthoyleneazoles, primary consideration was given to the study of polynaphthoylenebenzimidazoles, products of reaction between bis(*o*-phenylenediamines) and bis(naphthalic anhydrides), having the general formula

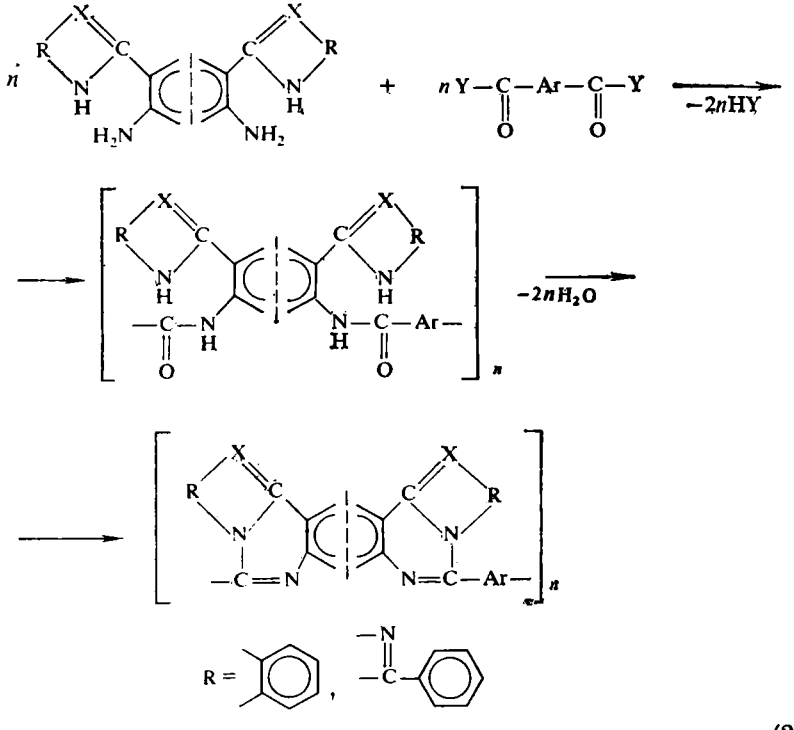


(23)

It will be noted that it was just in the case of the synthesis of polynaphthoylenebenzimidazoles [82] that high-molecular and well-cyclized polyheteroarylene systems were the first to be successfully obtained under conditions of the so-called precipitative polyheterocyclization. This process, involving precipitation of heterocyclic polymers from solutions in the course of polycyclocondensation, looks technologically attractive, eliminating the use of large volumes of solvents and precipitating agents for obtaining the desired polymers as fine powders specifically convenient for processing.

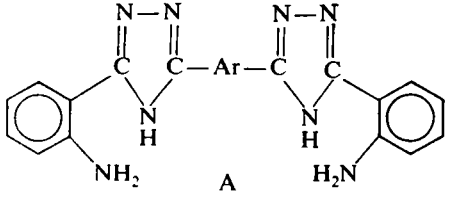
The most rigid-chain polynaphthoylenebenzimidazoles are substantially superior to conventional polyheteroarylenes as far as heat [85] and thermal [86] stability is concerned. On the basis of these polymers, the most thermostable polyheteroarylene fibres [87], thermostable films with superior mechanical properties [83], and high-temperature moulding materials have been obtained. One more trend in the chemistry of "ladder" polyheteroarylenes in the USSR concerns the development of polyazoloquinazolines by two-stage reactions of aromatic dicarboxylic acids, or derivatives thereof, with aromatic diamines containing aromatic heterocycles with labile

hydrogen atoms at *ortho* positions to amino groups [68, 69]. The process for producing these systems is basically identical to the general method for the synthesis of polybenzazoles (Eq. (3)). When using as monomers the diamines containing aromatic heterocycles with labile hydrogen atoms at *ortho* positions, the reactions proceed in a quite analogous manner, except that cyclodehydration processes yield highly condensed aromatic heterocycles responsible for a partially ladder structure of the resulting polyheteroarylenes [68, 69]:



(24)

In the series of the heterocycles that can be used potentially as *ortho*-substituents for aromatic diamines, the most widespread are benzimidazole and *s*-triazole cycles. In particular, as starting diamines, containing benzimidazole as *s*-triazole *ortho*-substituents, the compounds of the general formulas



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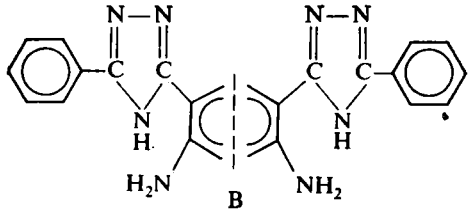
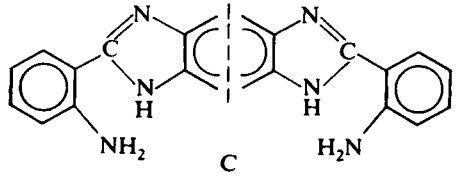
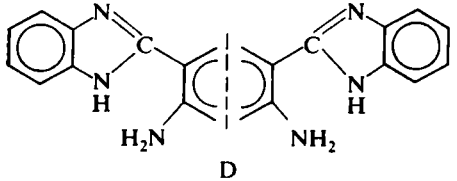


B (26)



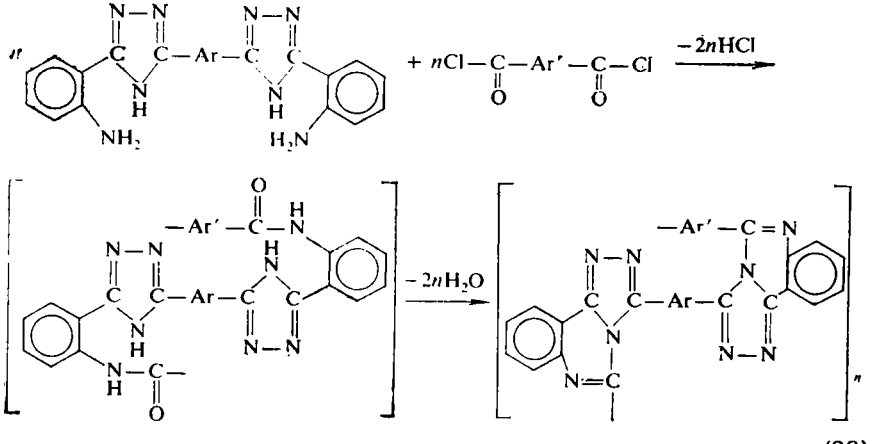
C (27)



D (28)

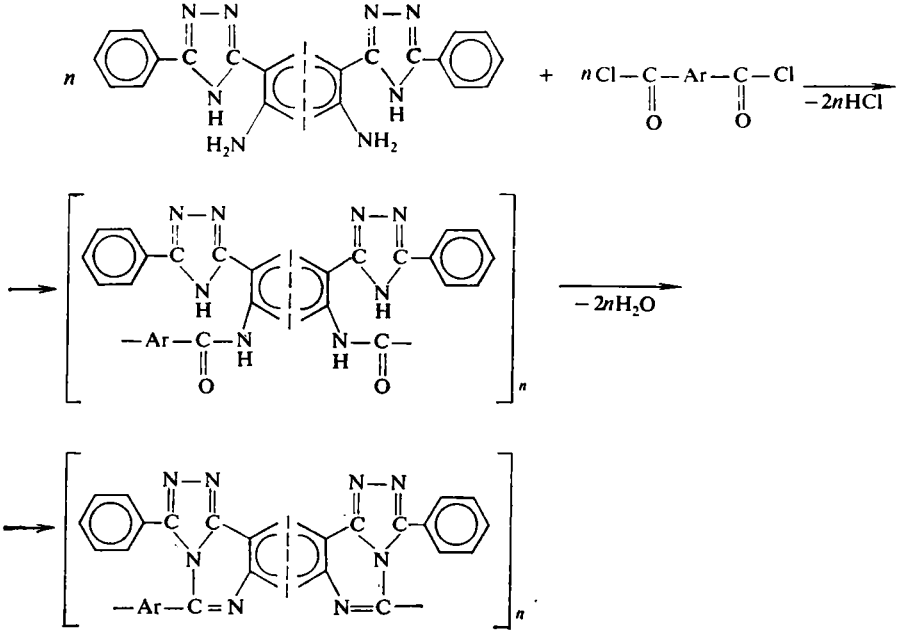
have been used [68, 69, 88-97].

All the four of the above types of diamines have been employed for obtaining partially ladder polyheteroarylenes. On the basis of A-type diamines, bis[5(2-aminophenyl)-1,2,4-triazole-3-yl]arylenes, poly-*s*-triazoloquinazolines [89-91] have been obtained. The most extensive use has been made of a two-stage method for the synthesis of these polymers which consists in mild reaction of bis[5(2-aminophenyl)-1,2,4-triazole-3-yl]arylenes with aromatic dicarboxylic acid dichlorides in hexamethylphosphamide [HMPA] followed by thermal cyclodehydration of the resulting poly(*o*-amidophenyl)-*s*-triazoles:



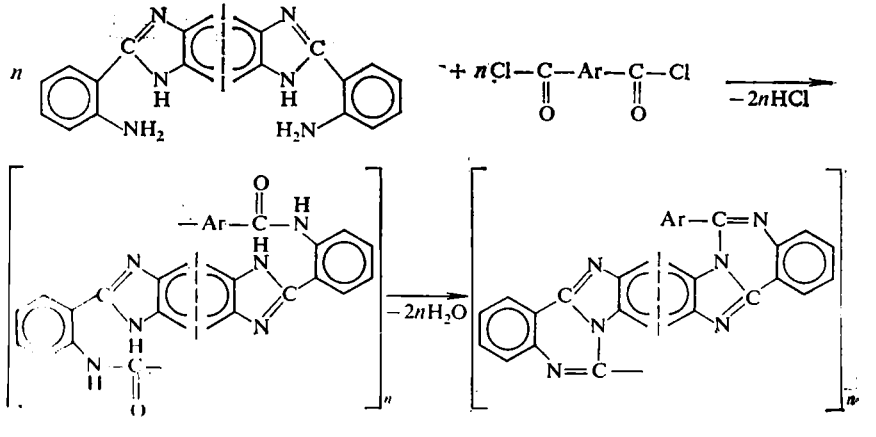
(29)

Partially ladder polymers, poly{benz[bis(*s*-triazoloquinazolines)]}, have been obtained from B-type diamines, 4,6-diamino-1,3-bis(5-phenyl-1,2,4-triazole-3-yl)benzene and aromatic dicarboxylic acid dichlorides [95-97]:



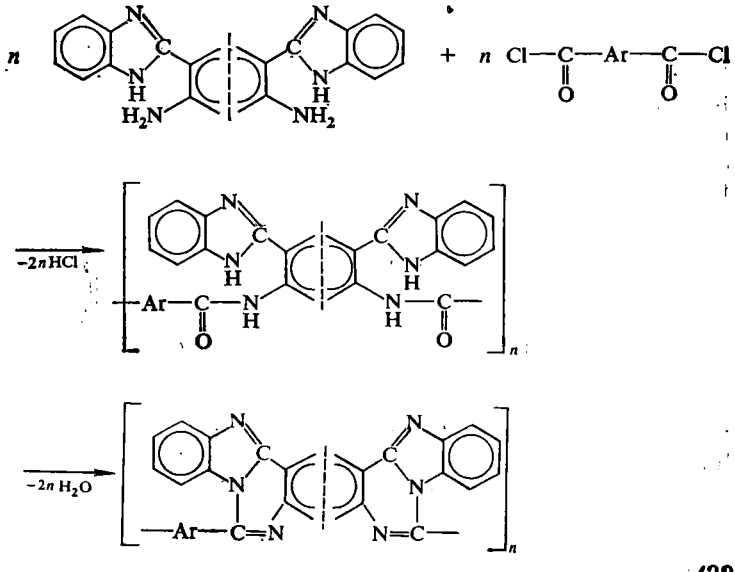
(30)

The same synthesis method was used to obtain partially ladder polyheteroarylenes from C- and D-type diamines. Starting from bis[2(*o*-aminophenyl)benzimidazole-6-yl]s and dicarboxylic acid dichlorides, polybenzimidazoloquinazolines have been obtained [94]:



(31)

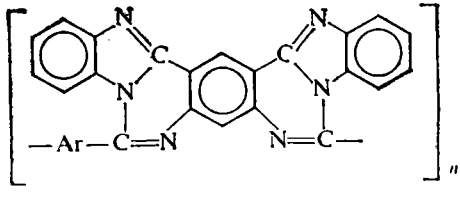
The use of D-type diamines as starting compounds resulted in the polybenzimidazoloquinazolines [88] and poly{benz[di(pyrimidobenzimidazoles)]} [92-97]:



(32)

All of the polyheteroarylenes prepared by this method have similar properties both at prepolymer and final steps. Ladder polyheteroarylenes of these types are usually soluble only in strong acids, i.e. sulphuric, trifluoroacetic, and PPA.

The high thermal stability of these systems is the most fully manifested in poly{benz[di(pyrimidobenzimidazoles)]}, polymers of the general formula

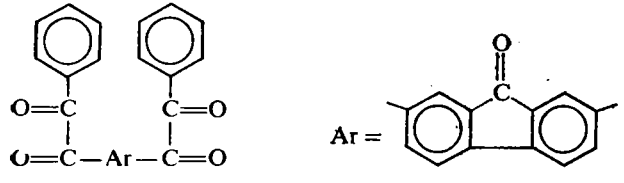


(33)

which are the products of reaction between 4,6-diamino-1,3-bis-(benzimidazole-2-yl)benzene and aromatic dicarboxylic acid dichlorides [92-98]. These polymers are between common polyheteroary-

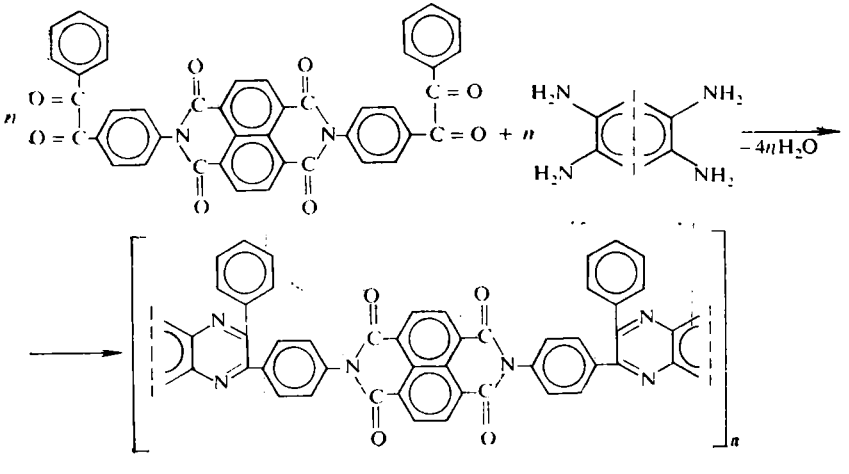
lenes and graphite with respect to thermostability. It should, however, be pointed out that high thermal properties of polybenzimidazoloquinazolines and poly{benz[di(pyrimidobenzimidazoles)]} have not yet been fully utilized in the development of new thermostable polymeric materials.

The concept of enhancing thermal and heat stability of polymers by introducing highly condensed heterocycles into the main polymeric chains has got considerable development in the USSR for enhancing thermal properties of polyphenylquinoxalines [99-101]. Studies into the use of tetraketones with high-condensed cycles of the exemplified formula [99]



(34)

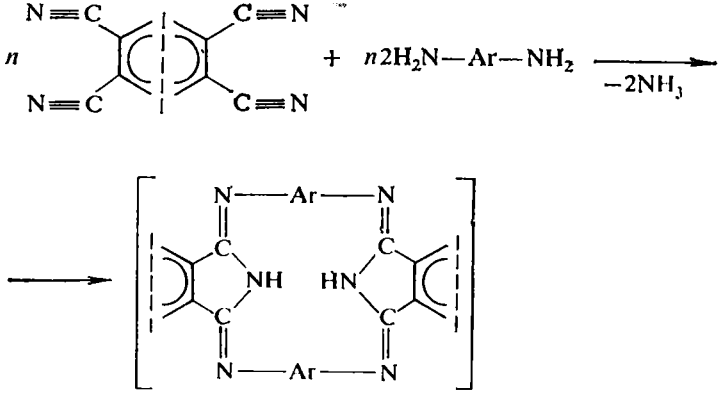
as monomers, demonstrated that this way is sufficiently effective for increasing the softening temperatures of polyphenylquinoxalines; however, this adversely affects the solubility and processability of the polymers, as well as their mechanical properties [13, 15, 99]. Better results have been achieved using, as a tetraketone, N,N′-bis(4-benzylyl)diimide of naphthalene-1,4,5,8-tetracarboxylic acid [100] which, when reacted with bis(*o*-phenylenediamines), yielded systems containing naphthylimide and phenylquinoxaline cycles



(35)

These polymers are soluble in *m*-cresol, N-MP, TCE/phenol mixture (3 : 1) and chloroform; they have high viscosities (η_{red} of 0.5% solutions is 1.7-2.2 dl/g), and this allows processing them into a variety of articles, and particularly, films with high mechanical characteristics [101].

An original approach to the synthesis of polymers with highly condensed heterocycles in the main macromolecular chains is represented by a series of investigations aimed at the synthesis of polymers with macroheterocycles in the main chains [102-110]. The synthesis of these polymers, called polyhexazocyclanes, is based on the polycondensation reaction of tetracarboxylic acid tetranitriles with diamines:

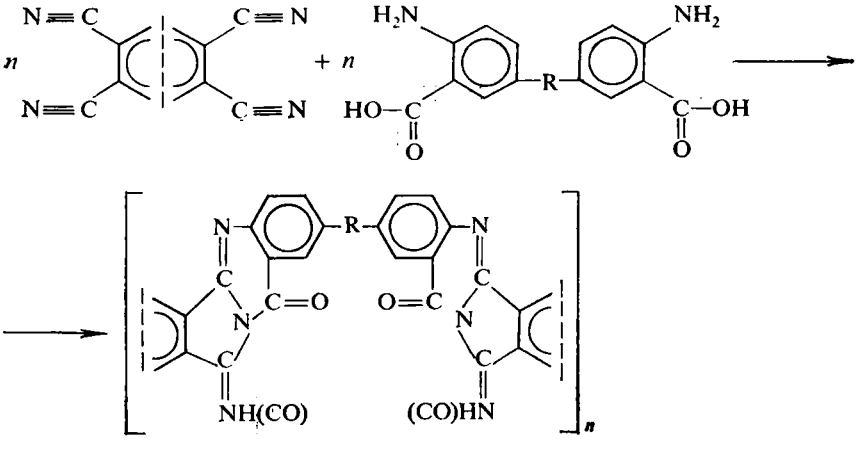


(36)

The investigations into the regularities of the synthesis of these systems and compounds simulating their structure demonstrated that a critical factor that determines the direction of the reactions and the structure of their products is the nature of the reaction medium; polyhexazocyclanes with a maximum content of macroheterocycles in the chains are formed when polycondensation is effected in phenols and cresols. The nature of the monomers used has a notable effect on the properties of the resulting polymers. For instance, the polyhexazocyclanes based on pyromellitic acid tetranitrile and diamines free from "hinged" groups and substituents are soluble only in sulphuric acid and do not soften without degradation. The use of compounds containing "hinged" groups and various (including "cardo") substituents as diamines yields polymers soluble in DMF, DMAA, DMSO, N-MP, etc.

A specific aspect of polyhexazocyclanes is that the thermostability inherent in their structure is not fully accomplished because ther-

mohydrolytic processes occur at relatively low (300-350 °C) temperatures. To avoid this disadvantage, the structure of polyhexazocyclanes has been modified so as to synthesize polymers containing isoindole cycles condensed with other heterocyclic fragments. This object was achieved by using, as tetranitrile comonomers, diamines with substituents at *ortho*-positions, capable of reacting with secondary amino groups of the isoindoline cycle [108]. Thus, the polycondensation of tetracarboxylic acid tetranitriles with bis(anthranilic acids) in PPA yielded polyisoindolequinazolines:



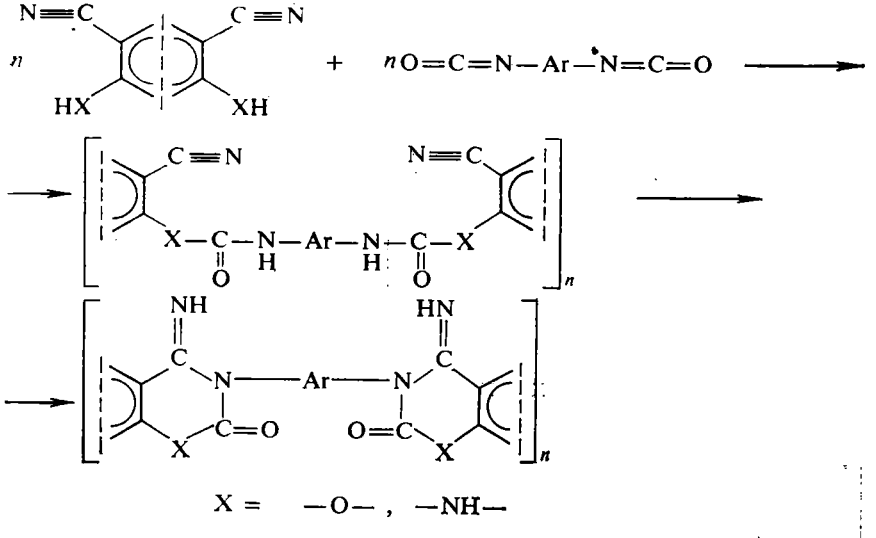
(37)

Other possible transformations of polyhexazocyclanes into highly condensed structures [111] involve reactions of isomerization cyclization, i.e. processes that are worth an independent thorough study.

4. ISOMERIZATION POLYCYCLIZATION

A basic advantage of isomerization polycyclization over the known two-stage method for the synthesis of polyheteroarylenes is the absence of volatile by-products at the stage of prepolymer cyclization, offering the possibility of processing them into bulky articles. Reactions of isomerization cyclization of cyan-containing prepolymers are among the most widely applied. Polyiminoquinazolones and polyiminobenzoxaziniediones synthesized from di[(*o*-amino)nitriles] and di[(*o*-oxy)nitriles] with diisocyanates followed by isomerization cyclization of the resulting polycyanurethanes and poly-

cyanureas [112-116] seem very attractive:

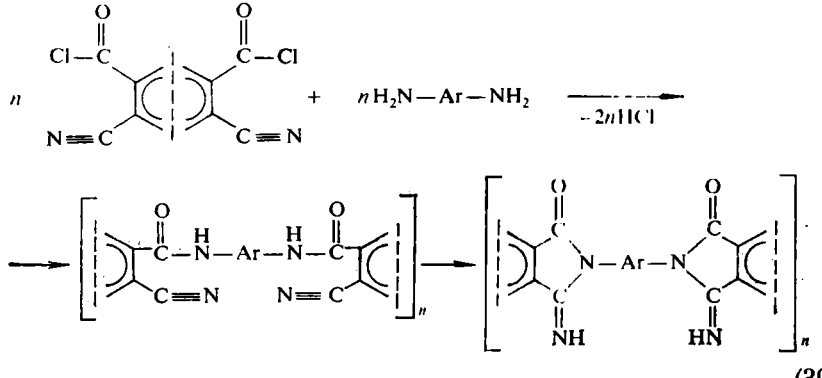


X = —O— , —NH—

(38)

The absence of volatile by-products, both during the formation of polycyanureas and at the stage of their cyclization, allows synthesis of these polymers without a solvent, directly from a monomer mixture, by the "reaction moulding" method [117]. Polyiminoquinazolones and polyiminobenzoxazinones offer high thermostability and are of significant interest as preparing thermostable adhesives, plastics, and laminates.

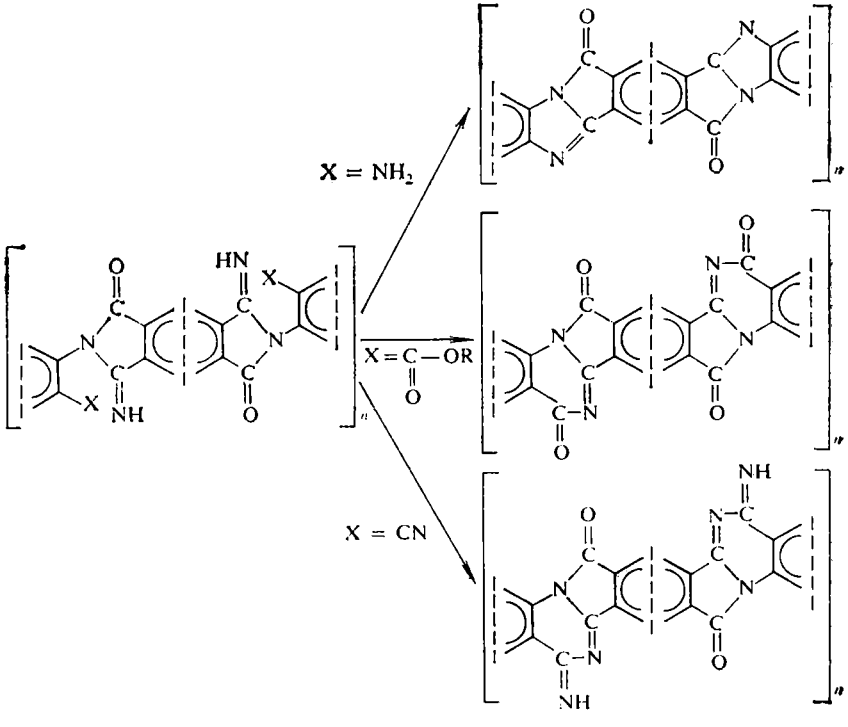
The same advantages are characteristic of polyiminoimides, polymeric products of reaction between diamines and dinitrilodicarboxylic acid dichlorides [115]:



(39)

The polyiminoimides are comparable with polyimides by the set of thermal and physicochemical properties, but they are superior to them due to the absence of volatile products during the cyclization process [115].

Using in this reaction, as comonomers of acid dichlorides of dinitrilodicarboxylic acids, bis(*o*-phenylenediamines), bis(anthranilic acids) and their diesters, as well as bis[*o*-amino(nitriles)], substituted polyiminoimides capable of further transformations [118-120] are being formed at first reaction stages according to the scheme



(40)

Among the processes represented by scheme (40), we would point out the reaction based on bis[*o*-amino(nitriles)] [120] which is a "double" isomerization cyclization proceeding without liberation of volatile by-products at both synthesis stages.

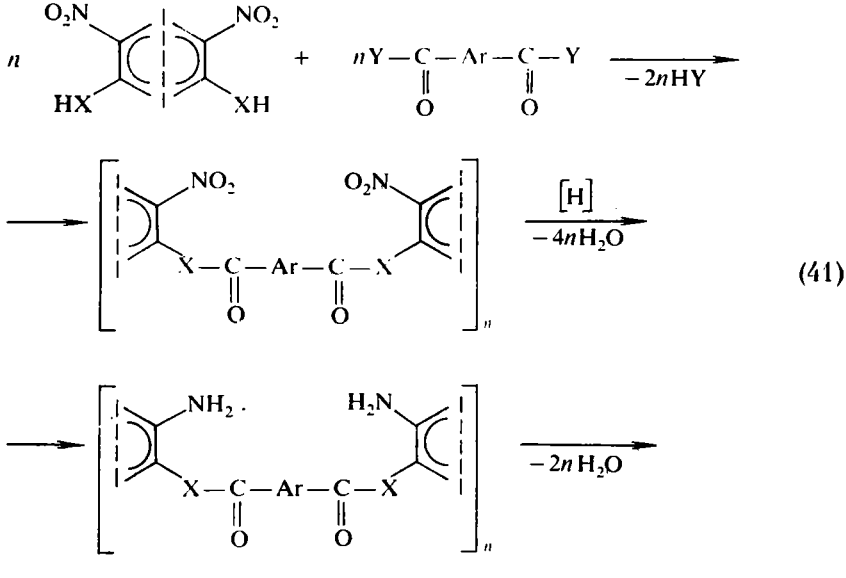
Along with the processes of isomerization polycyclization, the processes of reductive polyheterocyclization most largely used for the synthesis of polybenzazoles have made the object of thorough research in the USSR.

5. REDUCTIVE POLYHETEROCYCLIZATION

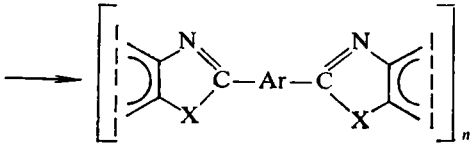
The most widely used processes for the synthesis of polybenzazoles described by Eq. (3) are reactions that involve the utilization of dicarboxylic acid dichlorides (Y=—Cl). This route is conventionally associated with the separation of prepolymers, poly(*o*-substituted)amides, thorough washing of polymers from HCl, which is a polycondensation by-product, and thermal polycyclodehydration of pure prepolymers.

The development of catalytic methods of polycondensation and polycyclocondensation [121] made it possible to develop a better technological approach to these systems, associated with catalytic cyclization of prepolymers directly in the reaction solutions using hydrogen chloride as catalyst, which is a by-product of the first process stage. Such an approach was realized to produce poly(N-phenyl)benzimidazoles [122] and polybenzoxazoles [123]; this approach looks promising, despite some doubts on the probabilities of achieving the balance of high molecular weights and high cyclization degrees in the target polybenzazoles.

The catalytic method of polybenzazole synthesis has found further evolution in a new general method for the synthesis of these systems, reductive polyheterocyclization [124, 125] proceeding according to the general scheme



(41)



X = —O—, —NH— ; Y = —Cl

It was used to advantage for the synthesis of polybenzimidazoles [126, 127] and polybenzoxazoles [128, 129]. The process is characterized by the fact that cyclodehydration reactions in polymeric chains occur immediately upon reduction of nitro groups to amino groups. It exhibits the following considerable advantages as compared with the conventional method for the synthesis of polybenzazoles by reaction of *o,o'*-disubstituted aromatic diamines with dicarboxylic acids or their derivatives according to scheme (3):

(1) the use of *o,o'*-dinitrosubstituted bifunctional compounds instead of *o,o'*-disubstituted aromatic diamines. Being intermediate products in the synthesis of the latter [21], the *o,o'*-dinitrosubstituted bifunctional compounds are more easily available, cheaper, and more stable than disubstituted aromatic diamines;

(2) the possibility of accomplishing the first process stage (the synthesis of *o*-nitrosubstituted polyamides and polyesters), without competitive acylation reactions of the two adjacent groups leading to gel formation, which allows the use of the most reactive dicarboxylic acid derivatives, and in particular, their dichlorides, as acylating agents;

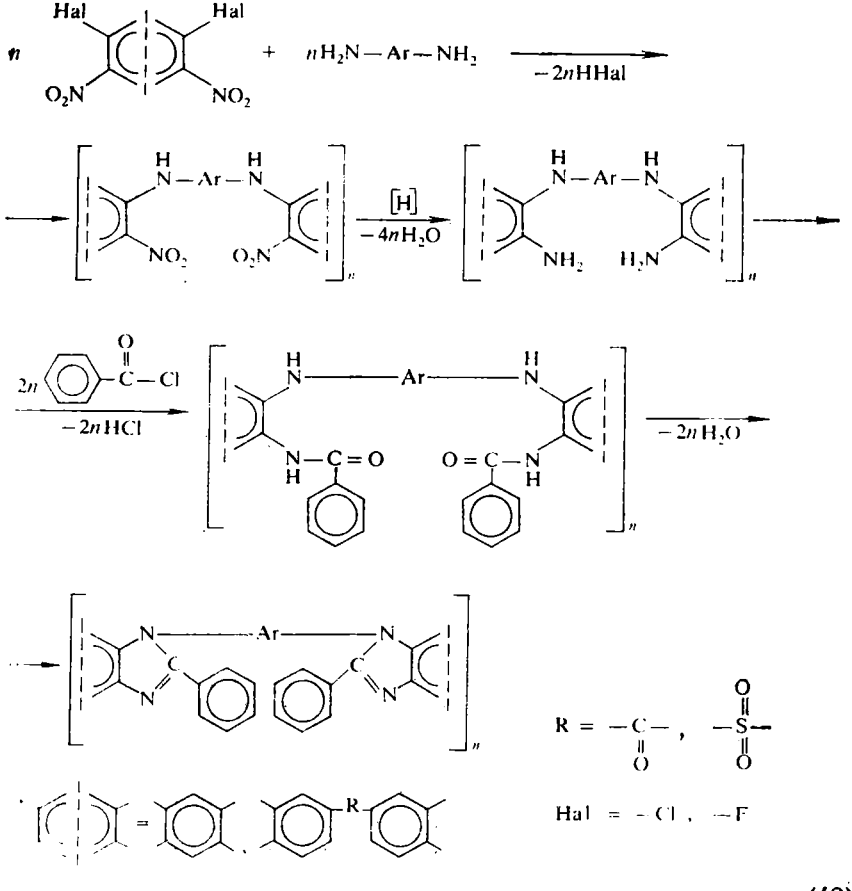
(3) the possibility of using hydrogen chloride liberated at the first stages of the processes, in combination with various metals, to reduce nitro groups to amino groups, and to catalyze the reactions of benzazole cycle formation [122, 123]. This last factor affords cyclization processes under mild conditions (160 °C), avoiding secondary processes, and to obtain polybenzazoles exhibiting a better solubility in organic solvents and better processability.

Along with the above-mentioned advantages, the reductive polyheterocyclization processes have the drawback of negative influence of nitro groups, which are strong electrone-acceptor substituents, on the reactivity of fragments participating in the polycondensation reaction, which becomes particularly obvious when using bis[(*o*-nitro)anilines] as monomers.

To overcome this shortcoming of reductive polyheterocyclization processes, still maintaining their above-mentioned merits, these reactions have been modified via the use of monomers containing functional groups activated by *o*-nitro substituents [124, 125].

The reactions of modified reductive polyheterocyclization are different from the foregoing processes in that the cyclization steps are

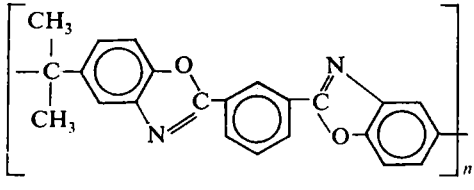
separated by one or more reactions (usually by acylation) from the stages of reduction of nitro groups to amino groups. All the processes of reductive polyheterocyclization proceed as continuous reactions in N-MP, an efficient solvent for heterochain and heterocyclic polymers, with reduced iron and hydrogen chloride as reducing agents, and hydrogen chloride as cyclization catalyst. An example of modified reductive polyheterocyclization is the synthesis of previously undescribed C-phenyl substituted polybenzimidazoles [124, 125, 130-133], which is based on reaction of activated bis(*o*-nitro)halogen arylenes with aromatic diamines, reduction of the resulting poly[(*o*-nitro)imines] to poly[(*o*-amino)imines], benzoylation of the latter and cyclization of the poly[(*o*-benzamido)imines] formed according to the scheme



(42)

Primary emphasis has been placed upon the synthesis of polymers from diphenylsulphone- and benzophenone-containing bis[(*o*-nitro)halogen]arylenes, as the "hinged" groups within these monomers are responsible for the solubility of all the intermediate and final polymeric systems in organic solvents and, correspondingly, for the possibility of accomplishing the polymer synthesis under homogeneous conditions. From the above consideration, 4,4′-diaminodiphenylmethane, 4,4′-diaminodiphenyloxide, and 4′,4″-diamino(hydroquinonediphenyl ether), as characterized by the highest basicity among diamines, could be most appropriately applied as aromatic diamines. The mild cyclization conditions, the presence of phenyl substituents, and a large amount of "hinged" groups in the main chains of polymers account for a good solubility of polybenzimidazoles in dipolar aprotic and phenolic solvents, while superior viscosity characteristics of these systems offer the possibility of processing them into articles with high mechanical properties.

Nowadays, the polymers of the structural formulas



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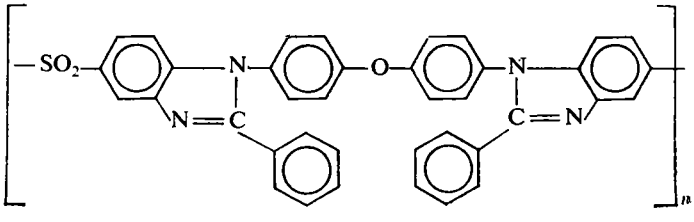
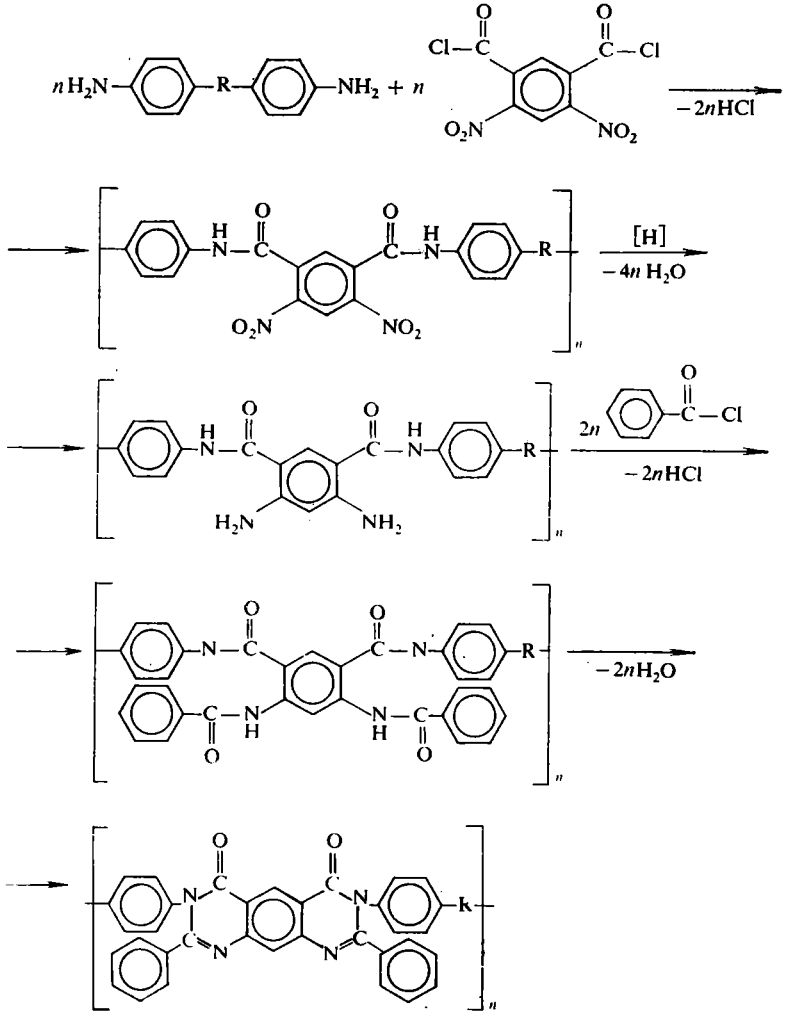


(44)

are, from the practical point of view, among the most promising.

The former system is based on 2,2′-bis(3-nitro-4-hydroxyphenyl)-propane, a product of direct nitration of bisphenol A used in the chemical industry for the production of polycarbonates and polysulphones, and on isophthaloyl chloride employed for the synthesis of polyamides. The latter system is based on 3,3′-dinitro-4,4′-dichlorodiphenyl sulphone, a product of direct nitration of 4,4′-dichlorodiphenyl sulphone, used in the synthesis of polysulphones, and on 4,4′-diaminodiphenyl oxide, used in the synthesis of polyimides. A combination of good solubility with superior viscosity characteristics of polymers in these systems makes it possible to convert them into various materials.

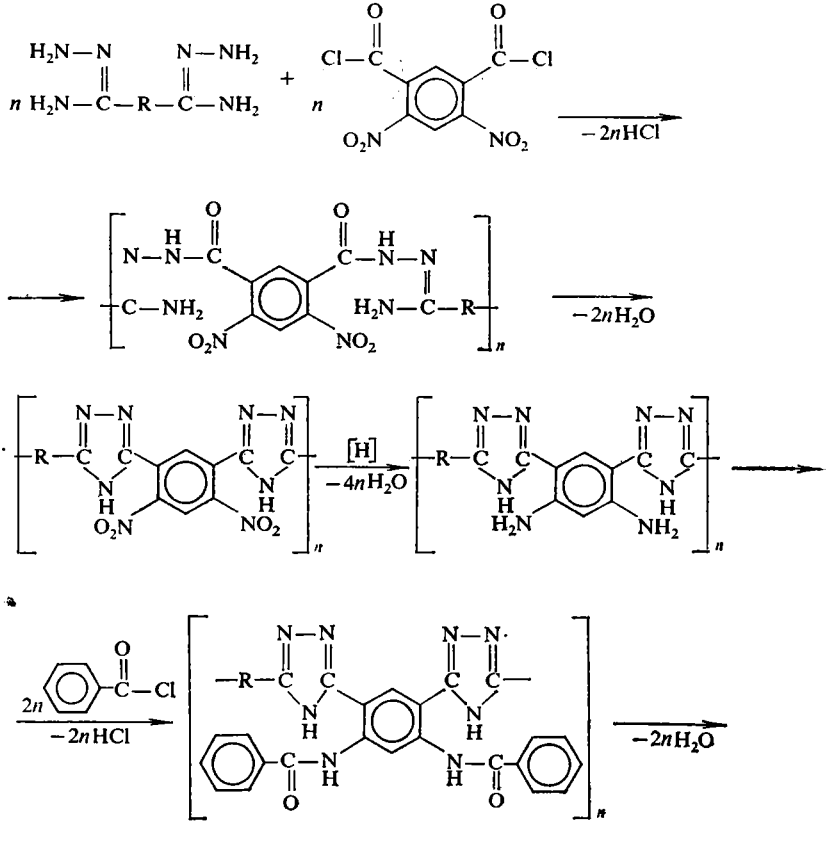
In addition to the synthesis of C-phenyl substituted polybenzimidazoles, another example of modified reductive polyheterocyclization is supplied by the synthesis of phenyl-substituted polyquinazolones [134], which is based on the reaction of aromatic diamines with 4,6-dinitroisophthalic acid dichloride with consequent reduction of the obtained poly[(*o*-nitro)amides] to poly[(*o*-amino)amides], benzoylation of the latter at free amino groups and catalytic polycyclization of the poly[(*o*-benzamido)amides] formed:

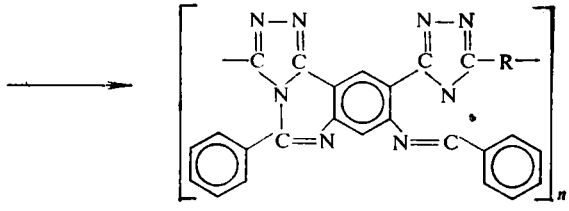


(45)

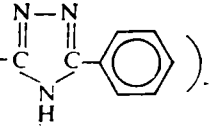
Synthesized polymers were soluble in strong acids, phenolic solvents, and, when heated, in dipolar aprotic solvents. According to dynamic and isothermal TGA data, the thermostability of these polymers is comparable with that of identical systems obtained by known methods [40].

High solubility of polyheteroarylenes synthesized by modified reductive polyheterocyclization made this process highly applicable to the synthesis of ladder polyheteroarylenes characterized by high heat and thermal stability but unsatisfactory processability [68, 69, 79, 135]. Phenylated poly{benz[di(*s*-triazolopyrimidines)]} were obtained by using dicarboxylic acid bis-amidrazones [14] as comonomers of 4,6-dinitroisophthalic acid dichloride [124, 125]:



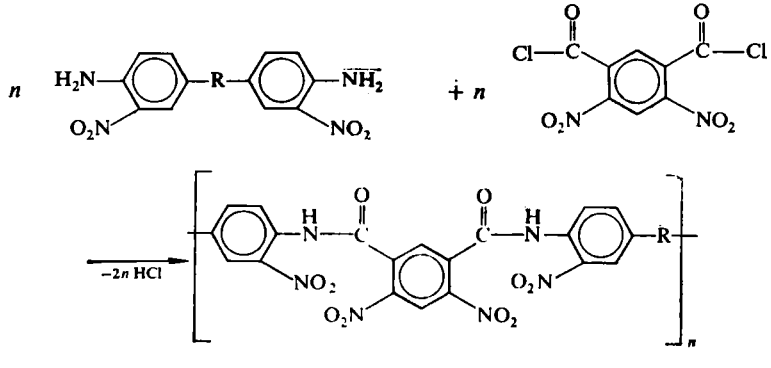


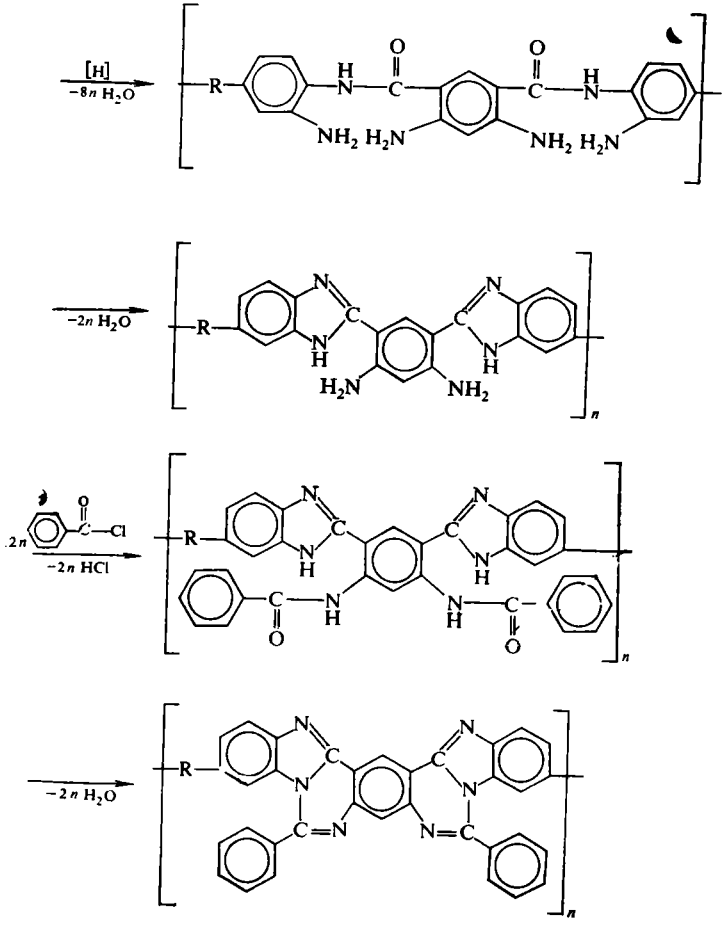
(46)

These polymers are isomeric to known systems [95] prepared by two-stage processes according to scheme (1)  .

The presence of side phenyl groups and mild polycyclization conditions determine the solubility of the resulting systems in acidic solvents (H_2SO_4, CF_3COOH), in a TCE/phenol (3 : 1) mixture, and a partial solubility in hot N-MP. A comparative study of thermostability of poly{benz[di(*s*-triazolopyrimidines)]} synthesized by modified reductive polyheterocyclization and by a two-stage method [95] using dynamic and isothermal TGA showed that these systems are comparable.

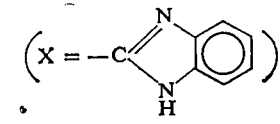
Besides the above-discussed modified reductive polyheterocyclization processes, the synthesis of polyheteroarylenes could be effected using the processes of combined reductive polyheterocyclization, some of the stages of which belong to the true reductive polyheterocyclization, and the others—to the reactions of modified reductive polyheterocyclization. The synthesis of poly{benz[di(pyrimidobenzimidazoles)]} based on bis[(*o*-nitro)anilines] and 4,6-dinitroisophthalic acid dichloride is a typical example of combined reductive polyheterocyclization [124, 125]:





(47)

As can be seen from scheme (47), the poly[(*o*-amino)phenyl]benzimidazole formation stage can be regarded as a true reductive polyheterocyclization, while the formation of the target poly{benz[di(pyrimidobenzimidazole)]} structure belongs to the processes of modified reductive polyheterocyclization. The polymers thus obtained reveal in the IR spectra neither unreduced nitro groups nor uncyclized fragments. Unlike the polymers obtained by the two-

stage method [95], according to scheme 

the poly{benz[di(pyrimidobenzimidazoles)]} prepared according to scheme (47) contain phenyl substituents which, combined with the mild conditions of polycyclization processes, make the polymers soluble in a TCE/phenol mixture (3 : 1), H_2SO_4, and CF_3COOH. The thermostability of poly{benz[di(pyrimidobenzimidazoles)]} is superior to that of the rest of polyheteroarylenes produced by modified reductive polyheterocyclization and are comparable under the isothermal TGA conditions with the polymers obtained by the two-stage method [95].

The above-discussed reactions of polyheteroarylenes synthesis do not use up the entire potential inherent in the modified and combined reductive polyheterocyclization, but nevertheless, are undoubtedly indicative of promising approaches to the preparation of both comparatively simple and complicated polymeric systems.

6. CONCLUSION

The above-discussed data demonstrate that Soviet researchers accomplished notable advances in all the fields of modification of polyheteroarylene performances, improvement of production methods, and development of novel polymeric structures. These achievements would undoubtedly represent an impetus and basis for further progress in the chemistry and technology of polyheteroarylenes.

References

1. V.V. Korshak, *Thermostable Polymers*, Khimiya, Moscow, 1969 (in Russian).
2. V.V. Korshak, *Chemical Structure and Thermal Properties of Polymers*, Nauka, Moscow, 1970 (in Russian).
3. A.H. Frazer, *High Temperature Resistant Polymers*, New York, John Wiley and Sons, 1968.
4. R.J. Cotter and M. Matzner, *Ring-forming Polymerization*, New York-London, Academic Press, 1972.
5. N.A. Adrova, M.I. Bessonov, L.A. Laius, and A.P. Rudakov, *Polyimides—a New Class of Thermostable Polymers*, Nauka, Leningrad, 1968 (in Russian).
6. C.E. Sroog, *J. Polymer Sci. Macromol. Revs.*, 2, 161 (1976).
7. A.L. Rusanov and I. Batirov, *Usp. Khimii*, 49, No. 12. 2418 (1980).
8. M.I. Bessonov, M.M. Koton, VV. Kudryavtsev, and L.A. Laius, *Polyimides—a Class of Thermostable Polymers*, Nauka, Leningrad, 1983 (in Russian).
9. I.E. Kardash and E.N. Teleshov, *Itogi Nauki. Khimiya i Tekhnologiya Vysokomolekularnykh Soedinenii*, VINITI, Moscow, 1971.

10. V.V. Korshak and M.M. Teplyakov, *J. Macromol. Sci.— Revs.*, C5, No. 2, 409 (1971).
11. A.A. Izyneev, M.M. Teplyakov, V.G. Samsonova, and A.D. Maksimov, *Usp. Khimii*, 36, No. 12, 2090 (1967).
12. V.V. Korshak and M.M. Teplyakov, in: *Progr. Polym. Chem.*, Nauka, Moscow, 1969, p. 198.
13. E.S. Krongauz, *Usp. Khimii* , 46, No. 1, 112 (1977).
14. A.L. Rusanov, *Usp. Khimii*, 43, No. 9, 1669 (1974).
15. E.S. Krongauz, *Vysokomolek. Soed.*, 24, No. 2, 227 (1984).
16. P.M. Hergenrother, *J. Macromol. Sci., Revs. Macrom. Chem.*, C6, 1 (1971).
17. A.Ya. Chernikhov, D.A. Solovykh, M.N. Yakovlev,V.A. Isaeva, N.V. Leont'eva, R.V. Markina, V.S. Popova, and B.E. Vostorgov, *Plastmassy*, No. 7, 40 (1977).
18. V.V. Korshak, G.L. Berestneva, and I.P. Bragina, *Dokl. Akad. Nauk SSSR*, 197, No. 3, 597 (1971).
19. V.V. Korshak, *Polymer Raznozvennost'*, Nauka, Moscow, 1977 (in Russian).
20. V.V. Korshak, *Usp. Khimii*, 42, No. 4, 695 (1973).
21. K. Stille, ed. *Condensation Monomers*, New York, Wiley-interscience division of John Wiley and Sons, 1972.
22. Ya.S. Vygodsky and S.V. Vinogradova, *Khimiya i Tekhnologiya Vysokomolekularnykh Soedinenii*, VINITI, Moscow, 1975, vol. 7, p. 14.
23. S.V. Vinogradova and Ya.S. Vygodsky, *Usp. Khimii*, 42, No. 7, 1225 (1973).
24. V.V. Korshak, S.V. Vinogradova, and Ya.S. Vygodsky, *J. Macromol. Sci., Rev. Macromol. Chem.*, C11, No. 1, 45 (1974).
25. V.V. Korshak, S.V. Vinogradova, and D.R. Tur, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 439 (1969).
26. S.V. Vinogradova, V.V. Korshak, and D.R. Tur, *Vysokomolek. Soed.*, B10, 396 (1968).
27. S.V. Vinogradova and D.R. Tur, *Vysokomolek. Soed.*, A15, 284 (1973).
28. S.V. Vinogradova, D.R. Tur, V.V. Korshak, and E.S. Krongauz, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 2827 (1968).
29. S.V. Vinogradova, Ya.S. Vygodsky, V.V. Korshak, N.A. Churochkina, and D.R. Tur, *Vysokomolek. Soed.*, A13, 1507 (1971).
30. V.V. Korshak, S.V. Vinogradova, D.R. Tur, and V.A. Khomutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2721 (1969).
31. E.S. Krongauz, A.L. Rusanov, T.L. Renard, *Usp. Khimii*, 39, 1591 (1970).
32. S.V. Vinogradova, V.V. Korshak, Ya.S. Vygodsky, *Vysokomolek. Soed.*, 8, 809 (1966).
33. S.V. Vinogradova, G.L. Slonimsky, Ya.S. Vygodsky, A.A. Askadsky, A.I. Mzhelsky, N.A. Churochkina, and V.V. Korshak, *Vysokomolek. Soed.*, A11, 2725 (1969).
34. V.V. Korshak, S.V. Vinogradova, Ya.S. Vygodsky, S.A. Pavlova, and L.V. Boiko, *Uzv. Akad. Nauk SSSR, Ser. Khim.*, 2267 (1967).
35. S.V. Vinogradova, Ya.S. Vygodsky, and V.V. Korshak, *Vysokomolek. Soed.*, A12, 1987 (1970).
36. S.V. Vinogradova, Z.V. Gerashchenko, Ya.S. Vygodsky, V.V. Korshak, and F.B. Sherman, *Dokl. Akad. Nauk SSSR*, 203, 821 (1972).
37. V.V. Korshak, S.V. Vinogradova, Ya.S. Vygodsky, and B.N. Yudin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1405 (1968).
38. S.V. Vinogradova, N.A. Churochkina, Ya.S. Vygodsky, G.V. Zhdanova, and V.V. Korshak, *Vysokomolek. Soed.*, A13, 1146 (1971).
39. V.V. Korshak, S.V. Vinogradova, Ya.S. Vygodsky, V.D. Vorob'yov, N.A. Churochkina, L.I. Chudina, and T.N. Spirina, *Vysokomolek. Soed.*, A16, 506 (1974).
40. V.V. Korshak, A.L. Rusanov, *Usp. Khimii*, 52, No. 5, 812 (1983).
41. S.V. Vinogradova, S.N. Salazkin, L.A. Beridze, A.I. Mzhelsky, A.A. Askadsky, G.L. Slonimsky, and V.V. Korshak, *Vysokomolek. Soed.*, A11, 27 (1969).

42. V.V. Korshak, A.L. Rusanov, S.Kh. Fidler, D.S. Tugushi, Yu.N. Margalitadze, R.G. Kakauridze, and S.N. Zinov'ev, *Plast. Massy*, No. 10, 28 (1984).
43. V.V. Korshak, A.L. Rusanov, A.M. Berlin, Z.B. Eig, G.S. Mironov, Yu.A. Moskvichev, and E.M. Alov, *Vysokomolek. Soed.*, B26, No. 9, 713 (1984).
44. V.V. Korshak, E.S. Krongauz, A.P. Travnikova, A.L. Rusanov, and R.D. Katsarava, *Dokl. Akad. Nauk. SSSR*, 196, 106 (1971).
45. V.V. Korshak, E.S. Krongauz, A.L. Rusanov, and A.P. Travnikova, *Vysokomolek. Soed.*, A16, No. 1, 35 (1974).
46. V.V. Korshak, E.S. Krongauz, A.L. Rusanov, and A.P. Travnikova, *Vysokomolek. Soed.*, A16, 1996 (1974).
47. V.V. Korshak, E.S. Krongauz, A.P. Travnikova, and A.L. Rusanov, *Macromolecules*, 7, 589 (1974).
48. P.N. Gribkova, A.P. Travnikova, E.S. Krongauz, A.L. Rusanov, and V.V. Korshak, *Vysokomolek. Soed.*, A17, No. 1, 18 (1975).
49. V.V. Korshak, A.L. Rusanov, R.D. Katsarava, F.F. Niyazi, and I. Batirov, *Vysokomolek. Soed.*, A16, 722 (1974).
50. V.V. Korshak, A.L. Rusanov, I. Batirov, R.D. Kazarawa, and F.F. Niyazi, *Faserforsch. u. Textiltechnik*, B29, Nos. 11-12, 649 (1978).
51. V.V. Korshak, V.A. Zamyatina, and N.I. Bekasova, *Organoboron Polymers*, Nauka, Moscow, 1975 (in Russian).
52. N.I. Bekasova, *Usp. Khimii*, 53, No. 1, 107 (1984).
53. V.V. Korshak, M.P. Prigozhina, and N.I. Bekasova, *Vysokomolek. Soed.*, A18, 827 (1976).
54. V.V. Korshak, S.A. Pavlova, P.N. Gribkova, T.N. Balykova, L.A. Mikadze, N.I. Bekasova, and M.P. Prigozhina, *Vysokomolek. Soed.*, A21, 304 (1979).
55. V.S. Voishchev, T.A. Burtseva, O.V. Voishcheva, P.M. Valetsky, and V.V. Korshak, *Vysokomolek. Soed.*, B18, 912 (1976).
56. V.S. Voishchev, P.M. Valetsky, V.I. Sidorenko, O.V. Voishcheva, S.V. Vinogradova, and V.V. Korshak, *Vysokomolek. Soed.*, A24, 2211 (1982).
57. A.I. Aksyonov, T.A. Burtseva, P.M. Valetsky, S.V. Vinogradova, and V.V. Korshak, *Vysokomolek. Soed.*, B22, 602 (1980).
58. V.V. Korshak, D.P. Kunchulia, and N.I. Bekasova, *Vysokomolek. Soed.*, A8, 1731 (1973).
59. V.V. Korshak, D.N. Kunchulia, and N.I. Bekasova, *Vysokomolek. Soed.*, A15, 2195 (1973).
60. V.V. Korshak, S.V. Vinogradova, L.A. Glivka, P.M. Valetsky, and V.I. Stanko, *Vysokomolek. Soed.*, A15, 1495 (1973).
61. M.A. Surikova, G.L. Berestneva, V.A. Khomutov, N.I. Bekasova, and V.V. Korshak, *Vysokomolek. Soed.*, B19, 597 (1977).
62. V.V. Korshak, N.I. Bekasova, M.A. Surikova, Yu.I. Tolchinsky, and I.V. Zhuravleva, *Vysokomolek. Soed.*, A19, 2768 (1977).
63. V.V. Korshak, E.S. Krongauz, N.I. Bekasova, L.G. Komarova, and N.M. Belomokina, *Dokl. Akad. Nauk SSSR*, 246, 114 (1979).
64. V.A. Ponomarenko, S.P. Krukovsky, and A.Yu. Alybina, *Fluorinated Heterochain Polymers*, Nauka, Moscow, 1973 (in Russian).
65. V.A. Ponomarenko, S.P. Krukovsky, and A.Yu. Alybina, in: *Advances in Synthetic Organoelement Polymers*, Moscow, Nauka, 1980, p. 154 (in Russian).
66. B.R. Livshits, S.V. Vinogradova, I.L. Knunyants, G.L. Berestneva, and T.Kh. Dymshits, *Vysokomolek. Soed.*, A15, 981 (1973).
67. V.V. Korshak, S.V. Vinogradova, Ya.S. Vygodsky, Z.M. Nagiev, Ya.S. Urman, S.G. Alekseeva, and I.Ya. Slonim, *Macromol. Chem.*, B184, 235 (1983).
68. V.V. Korshak and A.L. Rusanov, *J. Macromol. Sci.-Revs.*, C21, 275 (1982).

69. A.L. Rusanov, *Usp. Khimii*, 48, 115 (1979).
70. M.M. Tessler, *J. Polymer. Sci.*, A4, 2521 (1966).
71. M.M. Tessler, *ACS Polymer Prepr.*, 8, 152 (1967).
72. V.V. Korshak, A.L. Rusanov, I. Batirov, *Plast. Massy*, No. 8, 14 (1982).
73. V.V. Koršak, S.V. Vinogradova, and Ja.S. Vygodskiy, *Faserforsch. u. Textiltechn.*, 28, No. 9, 439 (1977).
74. Ya.S. Vygodsky, E.D. Molodtsova, S.V. Vinogradova, G.I. Timofeeva, S.A. Pavlova, and V.V. Korshak, *Vysokomolek. Soed.*, B21, 100 (1979).
75. V.V. Korshak, S.V. Vinogradova, Ya.S. Vygodsky, E.S. Krongauz, N.M. Kofman, H. Raubakh, H. Frommelt, D. Khain, and B. Falk. *Dokl. Akad. Nauk SSSR*, 236, 890 (1977).
76. V.V. Korshak, A.L. Rusanov, and I. Batirov, *Dokl. Akad. Nauk SSSR*, 240, No. 1, 88 (1978).
77. A.L. Rusanov, A.M. Berlin, S.Kh. Fidler, G.S. Mironov, Yu.A. Moskvichev, G.V. Kolobov, and V.V. Korshak, *Vysokomolek. Soed.*, A23, 1586 (1981).
78. M.M. Dashevsky, *Acenaphthene*, Moscow, Khimiya, 1966 (in Russian).
79. A.L. Rusanov, S.N. Leont'eva, and Ts.G. Iremashvili, *Usp. Khimii*, 46, 151 (1977).
80. A.A. Berlin, B.I. Liogon'kii, and G.M. Shamraev, *Usp. Khimii*, 40, 513 (1971).
81. V.V. Korshak, A.L. Rusanov, S.N. Leont'eva, and T.K. Jashiashvili, *Macromolecules*, 8, 582 (1975).
82. V.V. Korshak, A.L. Rusanov, A.M. Berlin, S.Kh. Fidler, and F.I. Adyrkhayeva, *Vysokomolek. Soed.*, A21, 68 (1979).
83. V.V. Korshak, A.L. Rusanov, A.M. Berlin, S.Kh. Fidler, B.R. Livshits, T.Kh. Dymshits, L.N. Silyutina, and V.F. Blinov, *Vysokomolek. Soed.*, A21, 657 (1979).
84. V.V. Korshak, A.L. Rusanov, R.S. Tabidze, B.R. Livshits, M.K. Kereselidze, and T.K. Jashiashvili, *Izv. Akad. Nauk GSSR, Ser. Khim.*, 8, No. 4, 320 (1982).
85. T.V. Todadze, A.A. Askadsky, G.L. Slonimsky, A.L. Rusanov, A.M. Berlin, S.Kh. Fidler, T.V. Lekae, I.A. Gribova, M.S. Todadze, O.V. Vinogradova, and V.V. Korshak, *Vysokomolek. Soed.*, A22, No. 3, 558 (1980).
86. V.V. Korshak, S.A. Pavlova, P.N. Gribkova, L.A. Mikadze, L.Kh. Plieva, A.L. Rusanov, and T.V. Lekae, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 6, 1381 (1977).
87. *Thermo-, Heat, and Fire Resistant Fibres*, ed. A.A. Konkin, Moscow, Khimiya, 1978 (in Russian),
88. V.V. Korshak, A.L. Rusanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1817 (1970).
89. V.V. Korshak, A.L. Rusanov, E.L. Baranov, Ts.G. Iremashvili, and T.I. Bezhuashvili, *Dokl. Akad. Nauk SSSR*, 196, No. 6, 1357 (1971).
90. V.V. Korshak, A.L. Rusanov, Ts.G. Iremashvili, I.V. Zhuravleva, and E.L. Baranov, *Macromolecules*, 6, 483 (1973).
91. V.V. Korshak, A.L. Rusanov, Ts.G. Iremashvili, I.V. Zhuravleva, and E.L. Baranov, *Vysokomolek. Soed.*, A16, 1516 (1974).
92. V.V. Korshak, A.L. Rusanov, L.Kh. Plieva, and E.S. Vulakh, *Dokl. Akad. Nauk SSSR*, 216, 1058 (1974).
93. V.V. Korshak, A.L. Rusanov, L.Kh. Plieva, and L.A. Mikadze, *Vysokomolek. Soed.*, A18, 1399 (1976).
94. V.V. Korshak, A.L. Rusanov, Ts.G. Iremashvili, L.Kh. Plieva, and T.V. Lekae, *Macromol. Chem.*, 176, 1233 (1976).
95. V.V. Korshak, A.L. Rusanov, L.Kh. Plieva, M.K. Kereselidze, and T.V. Lekae, *Macromolecules*, 9, 626 (1976).
96. V.V. Korshak, A.L. Rusanov, L.Kh. Plieva, M.K. Kereselidze, T.V. Le-

kae, and T.K. Dzhashiashvili, *International Symposium on Macromolecular Chemistry*, Summaries, Tashkent, 1978, vol. 3, pp. 42, 43.
97. V.V. Korshak, A.L. Rusanov, L.Kh. Plieva, M.K. Kereselidze, T.V. Lekae, and T.K. Dzhashiashvili, *Soobshch. Akad. Nauk GSSR*, 5, No. 1, 27 (1979).
98. V.V. Koršak, A.L. Rusanov, and L.Kh. Plieva, *Faserforschung u. Textiltechn.*, B28, 371 (1977).
99. V.V. Korshak, E.S. Krongauz, A.M. Berlin, N.M. Kofman, A.N. Novikov, and A.N. Moskal'chuk, *Vysokomolek. Soed.*, B16, 509 (1974).
100. V.V. Korshak, E.S. Krongauz, N.M. Belomoina, and L.L. Kashutina, *Vysokomolek. Soed.*, A19, 2760 (1977).
101. V.V. Korshak, E.S. Krongauz, A.M. Berlin, N.M. Kofman, A.N. Novikov, and A.N. Moskal'chuk, *Vysokomolek. Soed.*, B19, 730 (1977).
102. V.V. Korshak, S.V. Vinogradova, S.A. Siling, and L. Fedorov, *Dokl. Akad. Nauk SSSR*, 195, No. 5, 1113 (1970).
103. V.V. Korshak, T.M. Khrenkova, S.A. Siling, M.L. Chubarova, S.V. Vinogradova, and V.I. Kasatochkin, *Vysokomolek. Soed.*, A14, 701 (1972).
104. V.V. Korshak, S.V. Vinogradova, and S.A. Siling, *Vysokomolek. Soed.*, B15, 594 (1973).
105. S.V. Vinogradova, S.A. Siling, and V.N. Solov'ev, *Zh. Org. Khim.*, 10, 2437 (1974).
106. S.A. Siling, S.V. Vinogradova, and V.N. Solov'ev, *Macromol. Chem.*, 177, 1905 (1976).
107. V.V. Koršak, S.V. Vinogradova, S.A. Siling, V.N. Solov'ev, and L.M. Bronstein, *Faserforsch. u. Textiltechn.*, 26, No. 7, 318 (1975).
108. S.V. Vinogradova, S.A. Siling, I.I. Ponomarev, and V.V. Korshak, *Vysokomolek. Soed.*, A21, 138 (1979).
109. S.V. Vinogradova, S.A. Siling, V.N. Solov'ev, and V.V. Korshak, *Vysokomolek. Soed.*, A21, 288 (1979).
110. S.V. Vinogradova, V.V. Korshak, S.A. Siling, and V.N. Solov'ev, *J. Polymer Sci., Polymer Chem. Ed.*, 22, 1043 (1984).
111. I.I. Ponomarev, N.I. Vasyukova, S.A. Siling, B.V. Lokshin, S.V. Vinogradova, and V.V. Korshak, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 8, 1866 (1980).
112. A.I. Pravednikov, I.E. Kardash, E.N. Teleshov, and B.V. Kotov, *Vysokomolek. Soed.*, A13, 425 (1971).
113. I.V. Vasil'eva, E.N. Teleshov, A.N. Pravednikov, and L.D. Deryugina, *Dokl. Akad. Nauk SSSR*, 201, No. 4, 850 (1971).
114. I.V. Vasilieva, E.N. Teleshov, A.N. Pravednikov, and L.D. Deryugina, *Materials of International Symposium on Macromolecular Chemistry*, Helsinki, July 1972, vol. 2, p. 743.
115. E.N. Teleshov, R.M. Gitina, A.N. Flerova, E.L. Zaitseva, E.S. Botvinik, N.N. Ivanina, E.L. Gefter, I.V. Vasil'eva, N.N. Voznesenskaya, V.N. Yarosh, and A.N. Pravednikov, *Abstracts of XI Mendeleev's Conference on General and Applied Chemistry*, Alma-Ata, Nauka, 1975, vol. 2, p. 148 (in Russian).
116. A.Ya. Chernikhov and M.N. Yakovlev, in: *Results of Science and Techniques. Chemistry and Technology of High-molecular Compounds*, Moscow, VINITI, 1981, vol. 15, p. 73 (in Russian).
117. I.V. Vasil'eva, L.N. Kurkovskaya, A.N. Flerova, R.M. Gitina, E.L. Zaitseva, E.N. Teleshov, and A.N. Pravednikov, *Vysokomolek. Soed.*, A21, 1114 (1979).
118. N.N. Voznesenskaya, V.N. Yarosh, E.N. Teleshov, and A.N. Pravednikov, *Vysokomolek. Soed.*, A18, 140 (1976).
119. V.N. Yarosh, N.N. Voznesenskaya, E.N. Teleshov, and A.N. Pravednikov, *Vysokomolek. Soed.*, A18, 1360 (1976).

120. N.N. Voznesenskaya, V.N. Yarosh, A.N. Flerova, E.L. Zaitseva, E.N. Teleshov, and A.N. Pravednikov, *Vysokomolek. Soed.*, **B20**, 196 (1978).
121. V.V. Korshak, *Usp. Khimii*, **51**, 2096 (1982).
122. N.N. Voznesenskaya, V.I. Berendyaev, B.V. Kotov, V.S. Voishchev, and A.N. Pravednikov, *Vysokomolek. Soed.*, **B16**, No. 2, 114 (1974).
123. G.V. Kazakova, E.A. Seliverstova, S.V. Kachevsky, V.A. Isaeva, A.Ya. Chernikhov, A.L. Rusanov, and V.V. Korshak, *Liquid-phase Catalytic Reactions*, Alma-Ata, 1983, p. 160. *Abstracts of VI USSR Conference* (in Russian).
124. V.V. Korshak, A.L. Rusanov, and D.S. Tugushi, *Usp. Khimii*, **50**, 2250 (1981).
125. V.V. Korshak, A.L. Rusanov, and D.S. Tugushi, *Polymer*, **25**, No. 12, 1520 (1984).
126. V.V. Korshak, A.L. Rusanov, I.M. Gverdtsiteli, L.G. Kipiani, A.M. Berlin, D.S. Tugushi, and T.V. Lekae, *Dokl. Akad. Nauk SSSR*, **237**, No. 6, 1370 (1977).
127. V.V. Korshak, A.L. Rusanov, I.M. Gverdtsiteli, L.G. Kipiani, and D.S. Tugushi, *Vysokomolek. Soed.*, **A21**, 122 (1979).
128. V.V. Korshak, A.L. Rusanov, I.M. Gverdtsiteli, D.S. Tugushi, Z.Sh. Dzhaparidze, G.M. Tseitlin, and A.Ya. Chernikhov, *Dokl. Akad. Nauk SSSR*, **240**, No. 4, 873 (1978).
129. V.V. Korshak, A.L. Rusanov, D.S. Tugushi, Z.Sh. Dzhaparidze, I.M. Gverdtsiteli, A.Ya. Chernikhov, and G.M. Tseitlin, *Vysokomolek. Soed.*, **A21**, 1855 (1979).
130. I.M. Gverdtsiteli, D.S. Tugushi, L.G. Kipiani, Z.Sh. Dzhaparidze, A.S. Shubashvili, and A.L. Rusanov, *Abstracts of the International Symposium on Macromolecular Chemistry*, Tashkent, 1978, vol. 3, p. 18 (in Russian).
131. V.V. Korshak, A.L. Rusanov, I.M. Gverdtsiteli, D.S. Tugushi, and A.S. Shubashvili, *Dokl. Akad. Nauk SSSR*, **240**, No. 2, 346 (1978).
132. A.L. Rusanov, D.S. Tugushi, A.S. Shubashvili, I.M. Gverdtsiteli, and V.V. Korshak, *Vysokomolek. Soed.* **A21**, 1873 (1979).
133. V.V. Korshak, A.L. Rusanov, D.S. Tugushi, and A.S. Shubashvili, *Soobshcheniya Akad. Nauk GSSR*, **96**, No. 2, 341 (1979).
134. V.V. Korshak, A.L. Rusanov, D.S. Tugushi, M.V. Tsotadze, and I.M. Gverdtsiteli, *Dokl. Akad. Nauk SSSR*, **244**, 1348 (1979).
135. A.L. Rusanov, *Plast. Massy*, No. 7, 11 (1980).

6 Some Advances in the Chemistry of Organosilicon Polymers

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1. INTRODUCTION

The chemistry of organosilicon oligomers and polymers is one of the most intensively developing fields of polymer science in the Soviet Union. Its advancement, which has become especially apparent in recent years, arises both from the ever increasing demands of modern technology and from the solid foundation laid down, to a large extent, by basic works of Academician Andrianov. Scientific works by K. A. Andrianov, his ideas continue having a wholesome effect on the modern chemistry of organosilicon compounds.

One of the objectives of the present paper was to show the development of Andrianov's legacy in the studies made by his disciples and, using this example, to follow the trends in the further progress of the chemistry of organosilicon polymers and the ways of solution to the problems facing it. For space considerations the author did not seek to give full coverage to the literature; he merely attempted to collate and analyse recent studies in the field of the hydrolytic polycondensation of highly functional organosilanes and in synthesizing high molecular weight compounds by polymerization of cyclic siloxanes as well as some other types of organosilicon polymers.

2. HYDROLYTIC POLYCONDENSATION

Since 1937, when K.A. Andrianov discovered the first technologically valuable representatives of polyorganosiloxanes, produced by hydrolytic polycondensation (HP) [1, 2], this synthesis of organosilicon polymers has been a most important technique. Despite significant advances in this field, notably, in synthesizing ladder-type polyorganosilsesquioxanes [3-8], such important issues as the relationship between HP conditions and the structure of resulting primary, oligomeric and polymeric products, the ways of controlling HP and channelling it in a required direction as well as an increase in the stability of HP products in the case of highly functional monomers are still open.

In recent years the following major areas in further research on the HP of highly functional monomers have been recognized:

(i) defining the structure of labile hydrolysis products through stabilizing them by triorganosilylation;

(ii) investigating the structure of HP original products formed in partial hydrolysis conditions and their subsequent conversions into oligomers and polymers;

(iii) elucidating the effects of system's phase state on the direction of HP;

(iv) optimizing and mathematical modelling of HP within the framework of formally kinetic analysis.

Treated below are some of the findings obtained in the afore-mentioned areas.

2.1. Triorganosilylated Products of HP of Organosilicon Monomers

To yield and study the labile hydrolysis products of organosilicon monomers, an ever increasing use is made of their transfer to stable species by blocking the SiOH groups reacting the latter with triorganochlorosilanes (more often trimethylchlorosilane), triorganosilanols, or hexaorganodisiloxanes. Triorganosilylation has recently been employed to advantage to prepare several natural silicates [9-12].

Andrianov and co-workers have developed methods to synthesize soluble thermoreactive silsesquioxane oligomers on the basis of methyltrichlorosilane (MTCS) [13-15] and initiated studies into their structure using trimethylsilylation [15-17]. In Table 1 listed are the conditions of producing soluble oligomers on the basis of $MeSiCl_3$, and Fig. 1 depicts the chromatograms of trimethylsilylation products.

Table 1. Conditions Under Which Hydrolytic Polycondensation of Methyltrichlorosilane Is Conducted at 20 °C

Designation of HP product	Solvent	Water: MTCS, mole/mole	pH	Condensation time at 20 °C, min	Phase state of system
a	acetone	200 : 1	>1	4	heterogeneous
b	ditto	ditto	>1	1440	ditto
c	ditto	13 : 1	<1	15	homogeneous
d*	ditto	ditto	<1	15	ditto
e	ditto	ditto	<1	15	ditto
f	ditto	ditto	<1	0	ditto
g	diethyl ether	ditto	<1	15	heterogeneous

* Hydrolysis at a temperature of −15 °C

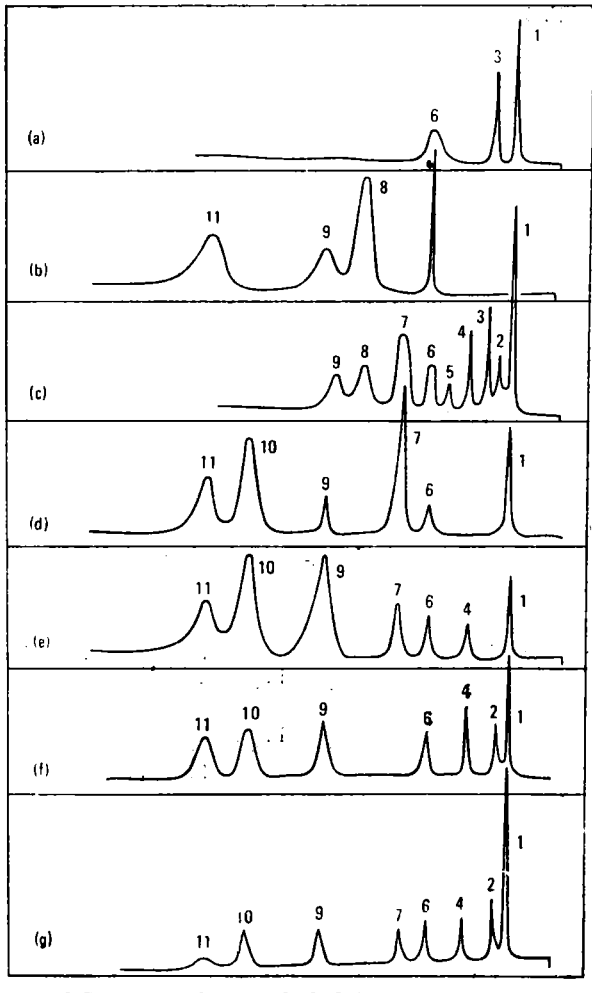
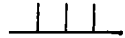
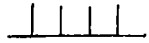
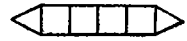
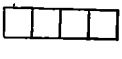
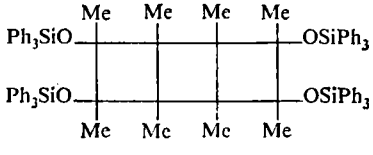


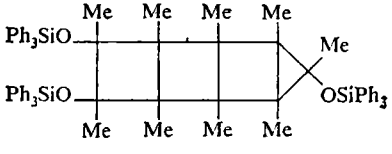
Fig. 1. GLC curves of trimethylsilylated derivatives of the HP of methyltrichlorosilane under various conditions (for designations of the GLC curves, see Table 1).

Peak numbers correspond to compounds of the following structure: *1*— , *2*—unidentified, *3*— , *4*— , *5*—  , *6*— , *7*— , *8*— , *9*—  , *10*—  , *11*— 

A question of principle concerns the absence of rearrangement processes of the siloxane skeleton under the conditions of the trimethylsilylation of the products of MTCS hydrolytic polycondensation, that is, the correspondence of the structure of the products identified by GLC to that of their precursors. Although no rigorous evidence of this correspondence has been given [16-20], still the data reported in the studies referred to can be looked upon as a good approximation towards evaluation of the structure of HP products. Four products of MTCS HP have been isolated as trimethylsilyl derivatives by high-vacuum distillation and their structure has been proved using elemental analysis, as well as the molecular-weight values, and IR spectra. The structure of a four-membered siloxane ring for one of them [19] gives rise to doubt.

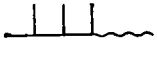
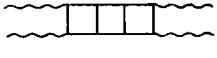
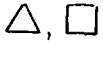
GLC analysis suggests that the products of MTCS HP would comprise 7 to 9 components characterized by constant retention times under certain conditions of chromatographing. The presence of compounds with three condensed 8-membered rings was demonstrated by conducting triphenylsilylation [16-17] and isolating two compounds by fractional precipitation





The structure of the above compounds was corroborated by the evidence from ^1H NMR spectra. The polycycle, methyl-T_8, described earlier was isolated from HP products with a large excess of water.

The remaining peaks on the chromatogram of Fig. 1 (with the exception of those assigned to preparatively isolated substances) were assigned from the assumption that retention time linearly depends on the molecular weight in the series of various homologues; linear


, polycyclic

and cyclic


The evidence obtained [16-20] has enabled some conclusions to be made about the composition and structure of MTCS HP products under various conditions. It was shown that in the first 15 minutes of the reaction $MeSi(OH)_3$ is present in the reaction mixture in perceptible amounts and is the most stable in ethyl ether. Strong dilution of the reaction mixture with water reduces the number of oligomeric products; reduced acidity favours a rise in the relative proportion of linear homologues.

What the reviewed cases of polycondensation have in common is its inhibition at the stage of formation of oligomeric products; attempts at preparing higher molecular weight compounds would result in gelatinization.

Similarly it was possible to identify several primary and oligomeric products during the cohydrolysis of MTCS and sodium silicate [17].

2.2. Basic Patterns Governing Formation and Composition of the Products of Partial Hydrolysis of Tetraethoxysilane

The partial hydrolysis of organochloro- and organoalkoxysilanes is frequently employed for synthesizing condensation primary products and preparing model siloxanes [21]. In connection with extensive applications found by tetraethoxysilane (TES), studies have been made into consistent patterns governing the formation of products of its partial hydrolysis which yields linear and cyclic ethoxysiloxanes:

$$EtO[Si(OEt)_2O]_x-Et\ (L-x),\quad [(EtO)_2SiO]_x\ (C-x)$$

where x corresponds, in the oligomer designation, to the number of atoms Si.

Figure 2 illustrates the content, as determined by the GLC method, of the linear and cyclic ethoxysiloxanes resulting from a homogeneous hydrolysis of TES in ethanol ($[TES]_0=2.3$ mole/litre) in the presence of 0.005 mole/litre of HCl as catalyst and with the equimolar ratio $n=TES/H_2O$.

The rate of TES consumption and conversion increase with n [25]; when $n\geqslant 0.8$, TES is consumed completely in the course of the reaction (Fig. 3). For each of the resulting ethoxysiloxanes there is an optimum value of n at which its yield is the highest (Fig. 3). In this case the content of linear homologues in the end products greatly differs from the statistical levels calculated by the Flory equation [28].

Theory deviates from experiment due to the formation of cycloethoxysiloxanes and different reactivities exhibited by TES and the ethoxysiloxanes produced on its hydrolytic polycondensation. The latter factor prevails at $n\leqslant 0.5$ when rings are still lacking in the reaction mixture.

Passing through the maximum of the dependence of the amount of the cyclic compounds yielded by TES partial hydrolysis (Fig. 2*b*) and a gradual attainment of stationary concentrations indicate that upon formation these compounds also enter into polycondensation. To bear it out, an attempt was made to polymerize cycloethoxysiloxanes in the presence of 0.05*N* HCl: it turned out that polymeri-

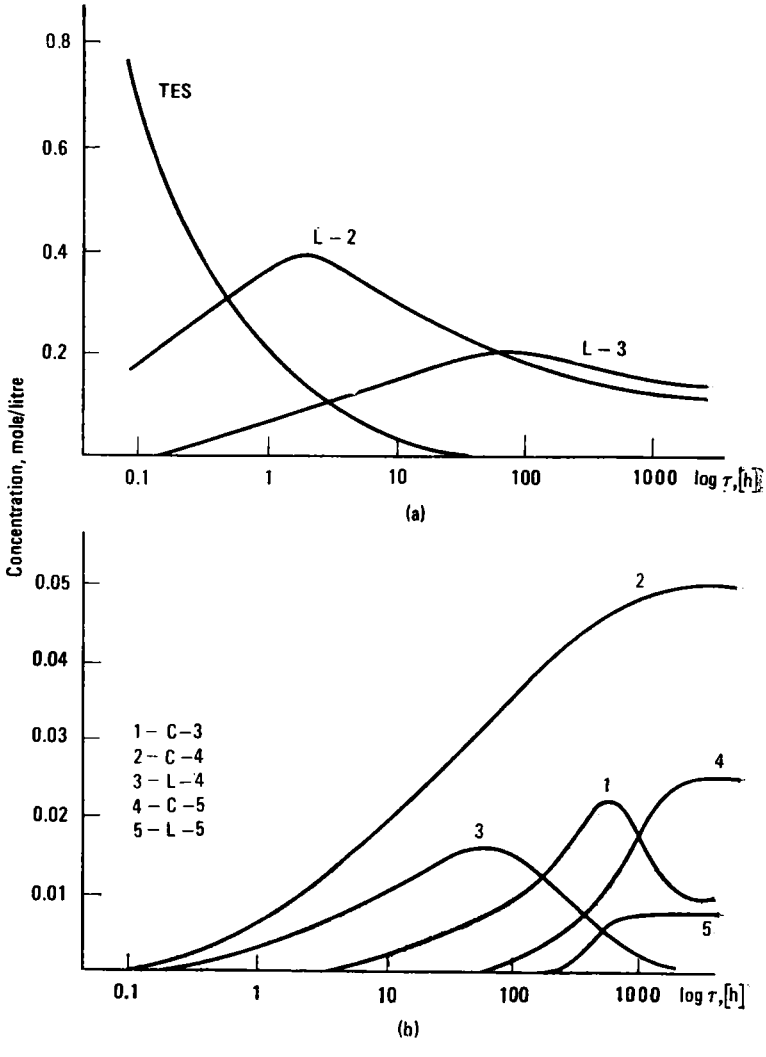


Fig. 2. Variations in the content of HP products of tetraethoxysilane with time at 20 °C, $n=1$, and [HCl] = 0.005 mole/litre

zation does not occur for a long time [25], whereas the said compounds are readily polymerized in the presence of bases.

Linear and cyclic ethoxysiloxanes with 2 to 5 Si atoms are the main HP products up to $n \leqslant 0.6$ (Fig. 4). With a further increase in n, the consumption of TES for their formation decreases due to the occurrence of higher molecular weight compounds in the reaction.

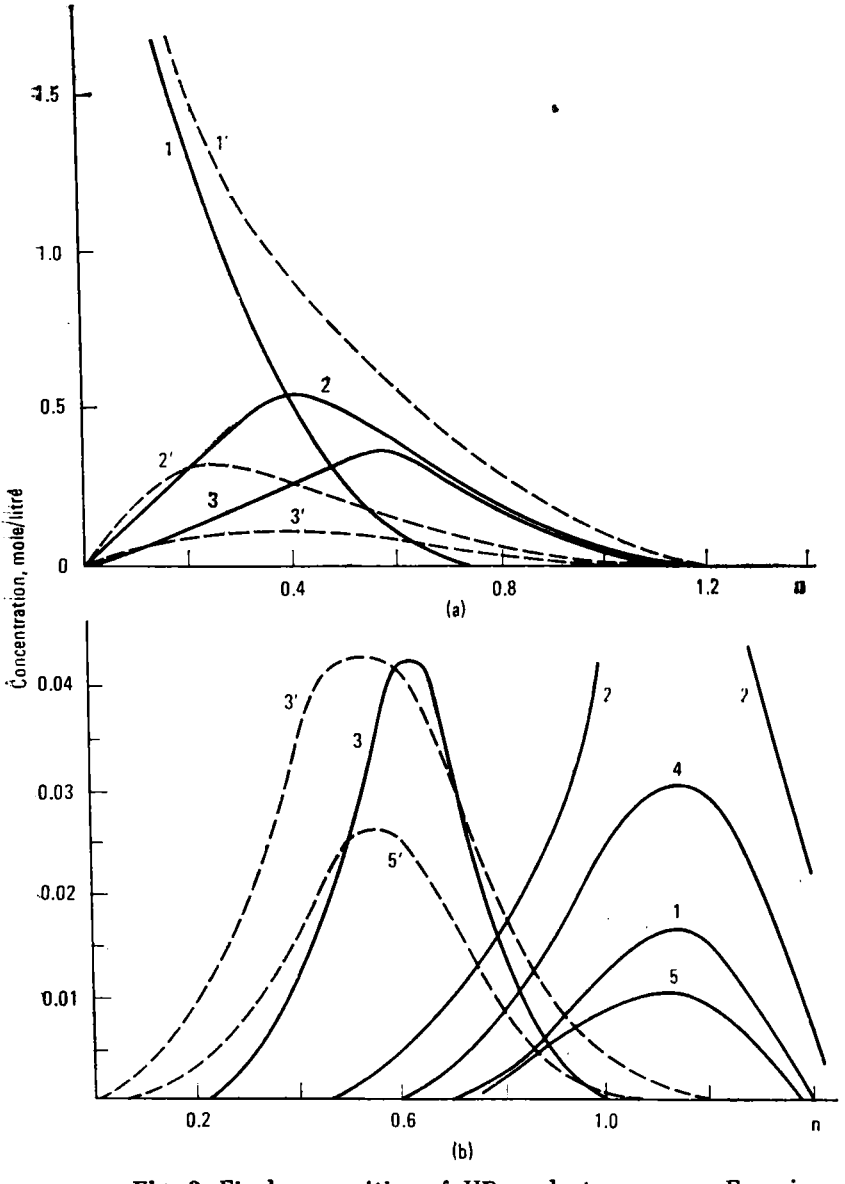


Fig. 3. Final composition of HP products versus n. Experimental results are shown by solid lines; Flory's calculations, by dashed lines
a: *1*—TES, *2*—L-2, *3*—L-3; *b*: *1*—C-3, *2*—C-4, *3*—L-4, *4*—C-5, *5*—L-5

mixture, and when $n=1.5$, it makes up merely 10%. A comparison of Figs. 2 and 3 suggests that the TES hydrolysis takes place predominantly at the initial HP stages, while the cocondensation of silanols with TES and ethoxysilanes proceeds at a lower rate ($k_1 > k_2$):

$$(EtO)_4Si + H_2O \xrightarrow{k_1} (EtO)_3SiOH + EtOH$$

$$\equiv Si-OEt + HOSi(OEt)_3 \xrightarrow{k_2} \equiv SiOSi(OEt)_3 + EtOH$$

Consequently, when $n < 0.5$, $(EtO)_3SiOH$ prevails in the reaction mixture at earlier stages, which yields linear ethoxysiloxanes, whereas when $n > 0.5$, sizable amounts of $(EtO)_2Si(OH)_2$ are produced,

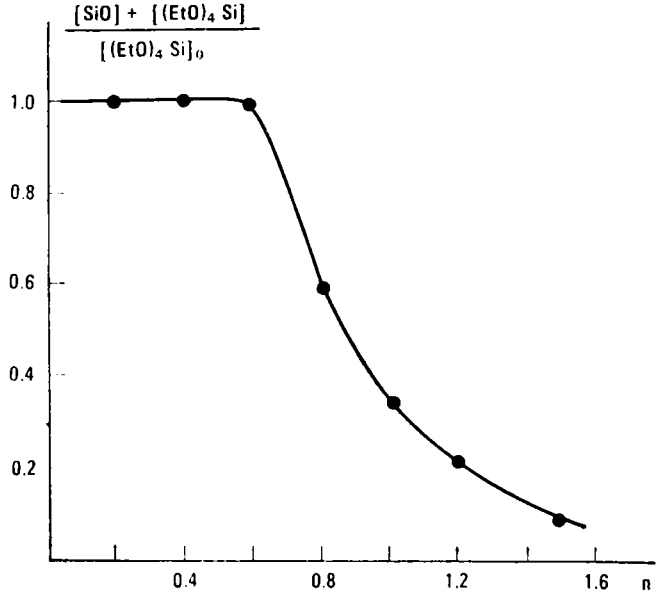


Fig. 4. Consumption of TES to form ethoxysiloxanes with the number of silicon atoms from 2 to 5

whose conversion leads to both linear and cyclic products. The reduced yield of cycloethoxysiloxanes when $n > 1.2$ is attributed to an increased portion of $EtOSi(OH)_3$, which should enhance the formation of branched polycyclic products.

The resulting oligoethoxysiloxanes contain the SiOH groups; they occur in the system starting from $n = 0.5$, their content reaches maximum when $n = 1$ and decreases slightly with a subsequent increase in n. A comparison of elemental composition, molecular weights,

the contents of lower ethoxysiloxanes, and the number of the SiOH groups was helpful in calculating the following data concerning the consumption of TES required for the formation of specific products [25]:

The value of n consumption of TES (%) to produce oligomers:	1.0	1.5
cyclic	15	6
linear at $x \leqslant 7$	21	—
linear at $x > 7$	64	94

When $n = 1.5$, functionality conversion amounts to 66%, which considerably exceeds critical conversion at the onset of gelatinization and equals 33% for TES. Therefore the macromolecules of the polymer thus formed contain a sizable amount of cyclic and polycyclic fragments.

The second important aspect of the TES HP, which becomes particularly apparent when $n=1.5$, is the discrepancy between the found (66%) and calculated conversions of the ethoxy groups (75%). With allowance made for the presence of the SiOH groups in the products, it is possible provided 9% of the starting water has not entered into the reaction and is in the reaction mixture in equilibrium:

$$\equiv SiOH + HOEt \rightleftharpoons \equiv SiOEt + H_2O$$

The third peculiarity of TES HP is the occurrence of disproportionation reactions. In view of the high sensitivity of the EtO—Si and SiOSi bonds to nucleophilic and electrophilic reagents, the role of disproportionation may be quite significant:

$$\equiv SiOSi\equiv + EtO-\overset{*}{Si}\equiv \rightleftharpoons \equiv SiOEt + \equiv SiO\overset{*}{Si}\equiv$$

It transpired that acids, HCl including, do not cause disproportionation and the latter proceeds in the presence of bases (Me_4NOH, Me_3SiONa) and some salts (KF, Me_4NF). The process shows up most vividly in the case of model compounds L-2 and L-3 [26] as well as mixtures of oligomeric ethoxysiloxanes [27]. Figure 5 demonstrates the disproportionation curves of L-2 and L-3, and Fig. 6 illustrates the effects of temperature on the time needed to attain equilibrium: Me_4NF and Me_3SiONa proved to be the most active catalysts [27].

For the reactions whereby all the linear products of disproportion-

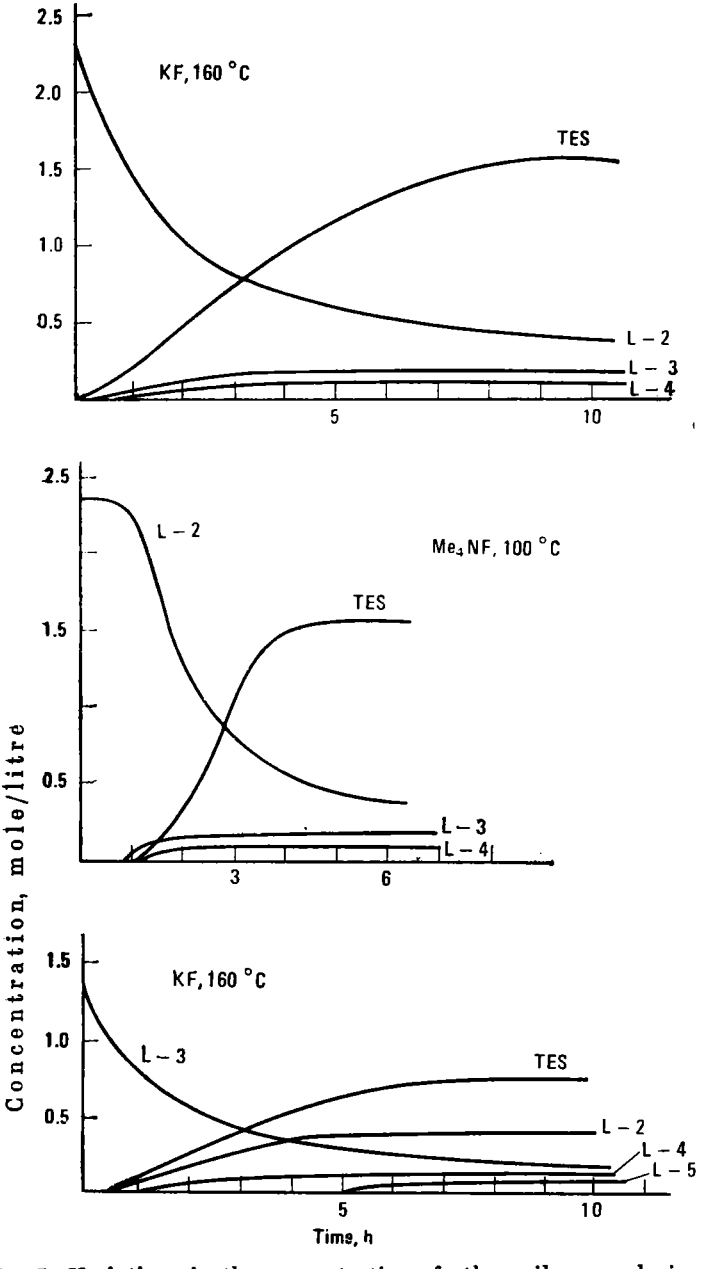


Fig. 5. Variations in the concentration of ethoxysiloxanes during disproportionation; [KF]=0.014, [Me_4NF]=0.013 mole/litre

ation are formed

$$2\text{L-2} \overset{K_1}{\rightleftarrows} \text{TES} + \text{L-3} \quad (1)$$

$$\text{L-2} + \text{L-3} \overset{K_2}{\rightleftarrows} \text{TES} + \text{L-4} \quad (2)$$

$$\text{L-2} + \text{L-4} \overset{K_3}{\rightleftarrows} \text{L-1} + \text{L-5} \quad (3)$$

$$\text{L-2} + \text{L-4} \overset{K_4}{\rightleftarrows} 2\text{L-3} \quad (4)$$

$$\text{L-2} + \text{L-5} \overset{K_5}{\rightleftarrows} \text{L-3} + \text{L-4} \quad (5)$$

$$\text{L-3} + \text{L-5} \overset{K_6}{\rightleftarrows} 2\text{L-4} \quad (6)$$

calculations were made, reasoning from their contents in equilibrium mixtures, of equilibrium constants, K_1-K_6, which agree fairly well with those computed for Flory's random process [28]:

Constant	K_1	K_2	K_3	K_4	K_5	K_6
Found	1.52	1.74	2.03	0.90	0.66	0.90
Calculated	1.56	1.76	2.06	0.89	0.73	0.89

The values of the given equilibrium constants are independent of temperature and this indicates that the enthalpy of disproportionation equals zero, and equilibrium is purely random.

Disproportionation oligomeric products of TES HP as $n = 1.2$ at 20 °C in the presence of 0.01 mole/litre of Me_4NOH [27] is characterized by a rapid exhaustion of the ethoxysiloxanes of cyclic structure (Fig. 7) which would also undergo polymerization under the conditions of disproportionation.

Check experiments showed that pure C-4 disproportionates practically instantaneously in the presence of Me_4NOH to form TES and linear ethoxysiloxanes with their content found being in agreement with that calculated according to Flory. Formation of TES from C-4 and other cyclic ethoxysiloxanes indicates that part of linear homologues must be branched or part of the rings must be incorporated into the resulting linear chains.

Evidence obtained from research into a partial hydrolysis of TES opens the way for controlling the composition and structure of HP end products by affecting the structure and relative content of the

oligomeric "blanks," formed at the first stage and the potential directions of their subsequent conversions—polycondensation, polymeri-

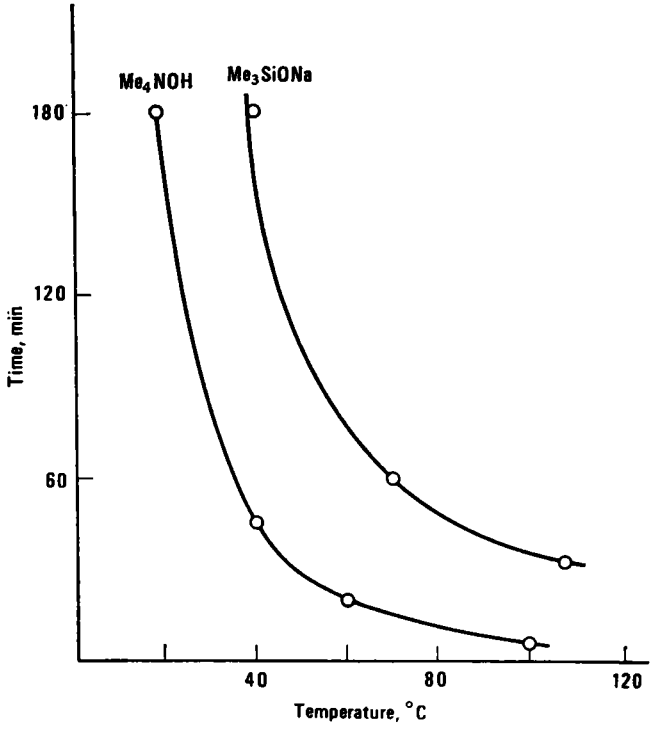


Fig. 6. The time needed to reach equilibrium as a function of temperature on disproportionation of L-2

zation, and disproportionation. The regularities referred to can also be employed in the hydrolytic polycondensation of other organosilicon monomers.

2.3. The Effects of the Phase State of the System on Hydrolytic Polycondensation

The occurrence of HP, as of any other polycondensation process [29], is greatly influenced by a variety of macroscopic factors, namely, the order of introduction and mixing of reactants, hydrodynamic parameters, the phase state of the reactive system, and the dynamics of its change as a consequence of the reaction. The effects of the above factors on the direction of the HP initial stage and the composition of the resulting products (the value of x) were

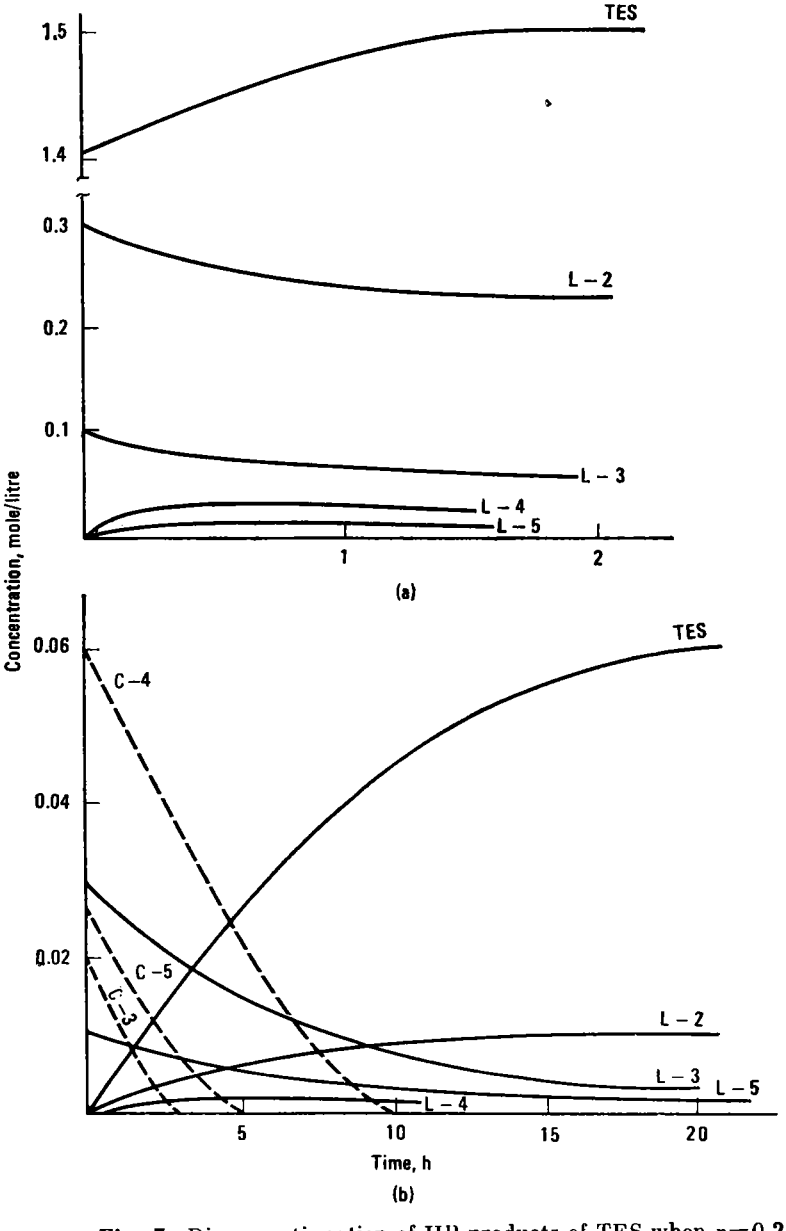
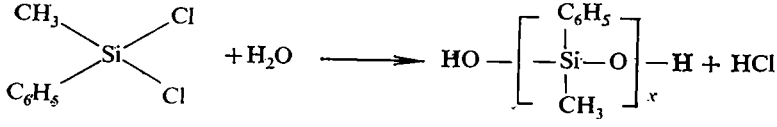


Fig. 7. Disproportionation of HP products of TES when $n=0.2$ (*a*) and 1.2 (*b*); $[Me_4NOH]=0.01$ mole/litre at 20 °C

discussed [30-32] for the case of the model hydrolysis of methylphenyldichlorosilane in the water-acetone mixture:



To avoid interaction of the resulting and starting substances, the process was carried out in a direct-flow reactor with intensive mixing and the residence time of the reaction mixture in the reactor being 1.5 min. The requisite value of pH was maintained by using an aqueous solution of ammonia for hydrolysis.

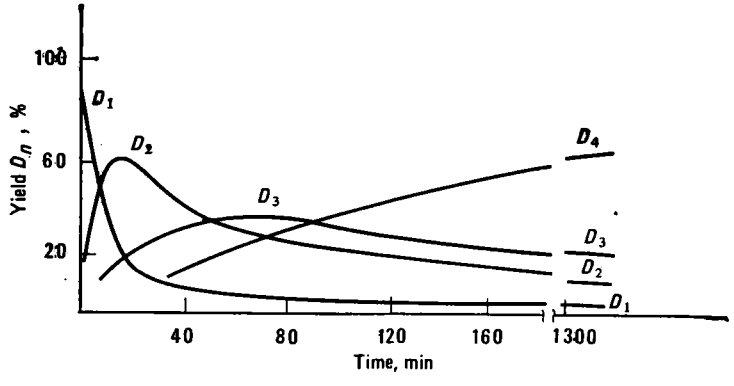


Fig. 8. Homocondensation of methylphenyldihydroxysilane (D_1) in the water-acetone mixture at [A]=39%, pH=7.9, and at 20°C, $[D_1]_0$=0.52 mole/litre

To elucidate the role of the homocondensation reaction of $Me(Ph)Si(OH)_2$ (D_1) in HP, a study was made into the rate of the process involved (Fig. 8). Calculation of the homocondensation rate constants for 20 °C yielded the following values:

pH	7.5	7.8	8.0	8.4	8.6	9.0
k, litre/mole·min	0.25	0.38	0.57	1.20	1.60	2.71

The activation energy of this reaction is 35-40 kJ/mole at 0-20 °C.

Linear siloxanes with $x \geqslant 5$ and cyclosiloxanes resulted from D_1 homocondensation were detected in the amount not exceeding 5%. The findings obtained suggest that under the selected conditions of HP, the homocondensation of methylphenyldihydroxysilane contributes insignificantly to the total balance of HP whereas the siloxanes determined in the reaction mixture result predominantly from

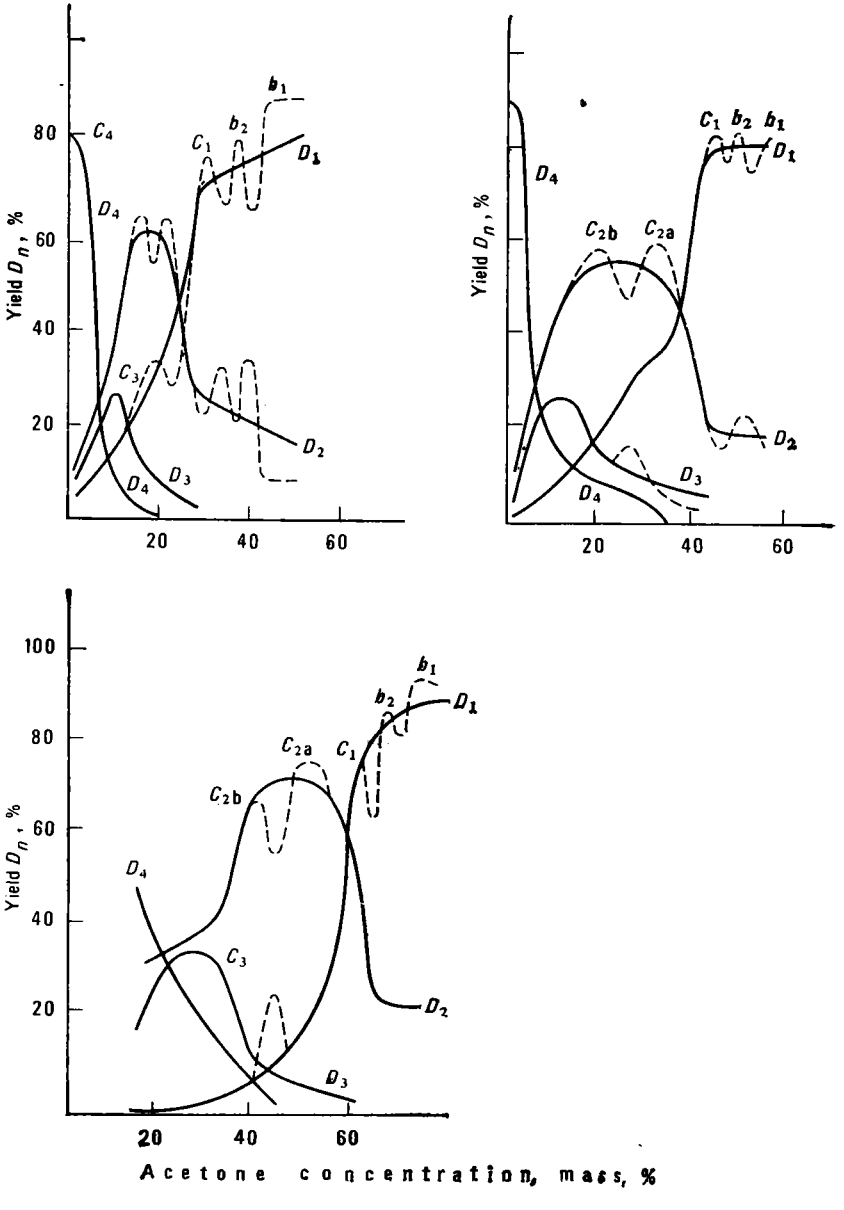


Fig. 9. Content of hydrolysis products of methylphenyldichlorosilane in the water-acetone mixture ("HP diagrams") as a function of the acetone amount in the mixture with water.

Concentration of MPDCS in the reaction mixture: *a*—13.6, *b*—23.5, *c*—44.0%

the heterofunctional condensation reaction:

$$\equiv Si-Cl + HO-Si\equiv \longrightarrow \equiv SiOSi\equiv + HCl$$

A dependence of the mass of products of methylphenyldichlorosilane (MPDCS) hydrolytic polycondensation on the amount of acetone in the reaction mixture is shown in Fig. 9. This plot was identified as an "HP diagram" [30]. The dependences demonstrated

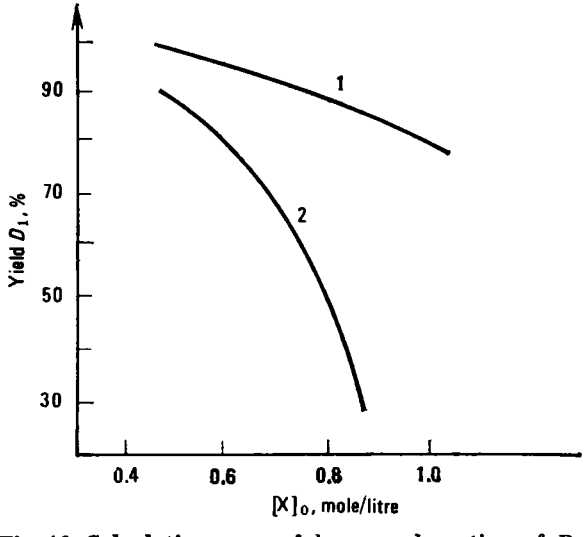


Fig. 10. Calculation curve of homocondensation of D_1 (*1*) and alterations in the yield of D_1 on the hydrolytic polycondensation of MPDCS as a function of the initial concentration of the latter in the reaction mixture (*2*). HP conditions: pH = 8, m = 40, t = 20 °C

are characterized by a drastic change in the HP selectivity with respect to D_1 yield, as the proportion of acetone decreases, and by the presence of inflections C_1 for its specific content $[A_{C_1}]$. The contribution of this reaction to changes in the composition of HP products over the 0-60% range of acetone concentration was evaluated using the constants and the value of the homocondensation activation energy referred to above. The calculation corroborated the above conclusion [30] that homocondensation does not cause a sharp increase in the yield of linear homologues with a decreasing amount of acetone (Fig. 10). Similar HP diagrams were obtained on varying in the reaction mixture of the amount of chlorosilane [X] over the range of 5-70%.

The experimental evidence obtained was rationalized reasoning from the laws of phase equilibrium in a liquid-liquid system [30,

31]. The reaction three-component system MPDCS-acetone-water can be classified as the heterogeneous systems of the first type, that is, those having two pairs of mutually soluble and one pair mutually insoluble components. In the initial state (after mixing but prior to reacting), the system has two fields of the reactant ratio, homogeneous and heterogeneous (Fig. 11). Proceeding from the diagram presented, a change in the composition of HP products with a reduced

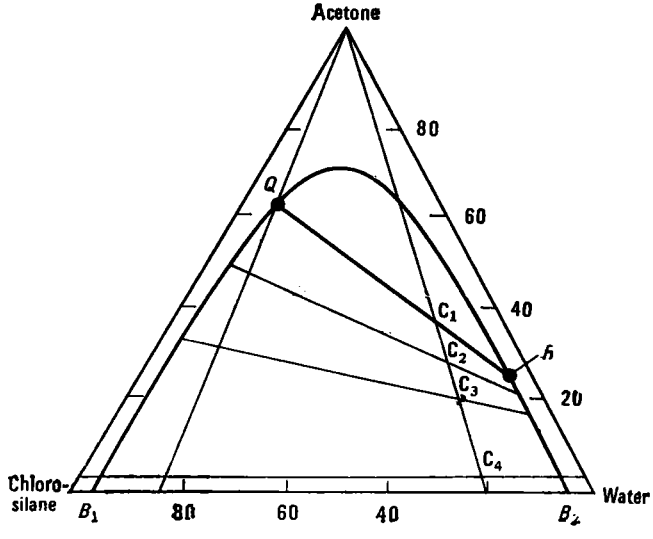


Fig. 11. Expected initial phase equilibrium in the MPDCS-water-acetone system

amount of acetone was explained as follows. The starting heterogeneous mixture C_{1i} of specified composition is separated into two coexisting phases, "chlorosilane" ($m=H_2O/MPDCS<2$) and aqueous ($m\gg2$), with each of the phases containing all the three parent components. Because of the lack of water in the "chlorosilane" phase, Q (Fig. 11), partial hydrolysis and heterofunctional condensation occur to yield α,ω-dichlorosiloxanes (subsequently, α,ω-dihydroxysiloxanes). Due to excess water, the aqueous phase, R, yields predominantly D_1. Consequently, the relationship between D_1 and oligosiloxanes will depend on the phase distribution of chlorosilane, which is determined by the mass of phases (x and y) and the concentration of MPDCS in them, $[X]_r$ and $[X]_q$. The amount of chlorosilane in phases Q and R (Fig. 11) is defined by the product of its concentration by the phase mass: in phase Q_j—$[X]_q \cdot x_{ij}$; in phase R_j—$[X]_r \cdot y_{ij}$. Then selectivity of the HP process with reference to D_1

can be derived from the expression

$$D_1 = \frac{[X]_r \cdot y_{ij}}{[X]_r \cdot y_{ij} + [X]_q \cdot x_{ij}} \quad (7)$$

or

$$D_1 = \frac{1}{1 + \frac{1}{K_d} \cdot \frac{x_{ij}}{y_{ij}}} \quad (8)$$

where K_d is the coefficient of chlorosilane distribution in existent phases R and Q; $K_d = [X]_r/[X]_q$.

As is seen from Fig. 11, as the content of acetone in the reaction mixture decreases as compared with its amount at point C ($[A_C]$), the chlorosilane concentration in aqueous phases changes only slightly whereas in chlorosilane phases Q it varies from 30 to 98%, which drastically lowers K_d and, according to formula (8), brings about a sharp drop in the yield of D_1 and an increase in the relative share of oligosiloxanes.

The HP diagram was experimentally borne out [30, 31] on the assumption that points C_{1i}, ($C_{1,1}$, $C_{1,2}$, $C_{1,3}$, etc.) correspond to "chlorosilane" phase Q_j with $m \leqslant 2$ and should therefore fall in the same straight line, viz. a node connecting the coexistent phases. An assumption was also made that the representative points in the HP diagrams, b_i, correspond to the transition of the system from the homogeneous to the heterogeneous region, and their sum total for different [X] should yield a binodal curve.

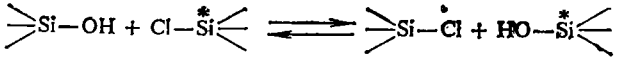
Figure 12 illustrates part of the diagram of the state of the MPDCS-water-acetone reaction mixture, obtained on the assumption referred to. Experimental evidence for constructing the dependences on Fig. 12 was derived from the "HP diagram" over the range $[X]_i =$ =5-73% and [A]=0-90%.

It has not been practicable as yet to determine experimentally the composition of aqueous and chlorosilane phases; for this reason Fig. 12 diagrammatically illustrates the nodes of phase equilibrium of the MPDCS-water-acetone system, produced by connecting the coordinates of like representative points C_{ji} characterized by a well-defined "chlorosilane" phase. A certain curvature of the nodes of phase equilibrium at $[X]_i > 45\%$ is a consequence of the salting-out effect of ammonium chloride [30, 32].

The "HP diagrams" of alkaline and acid hydrolysis are identical and this suggests that the composition of MPDCS HP products does not depend on the pH of the medium. Consequently, the growth of a siloxane chain occurs according to the heterofunctional condensation of the compounds R_2SiCl_2, $R_2Si(OH)Cl$, and $R_2Si(OH)_2$ as well as oligomers containing the SiCl and SiOH bonds.

Apart from the reaction in question, during the hydrolytic poly-

condensation of organochlorosilanes, there may take place an exchange reaction of functional groups



whose equilibrium constant value is dependent upon the number and species of the organic radicals bound to the Si atom [33]. This reac-

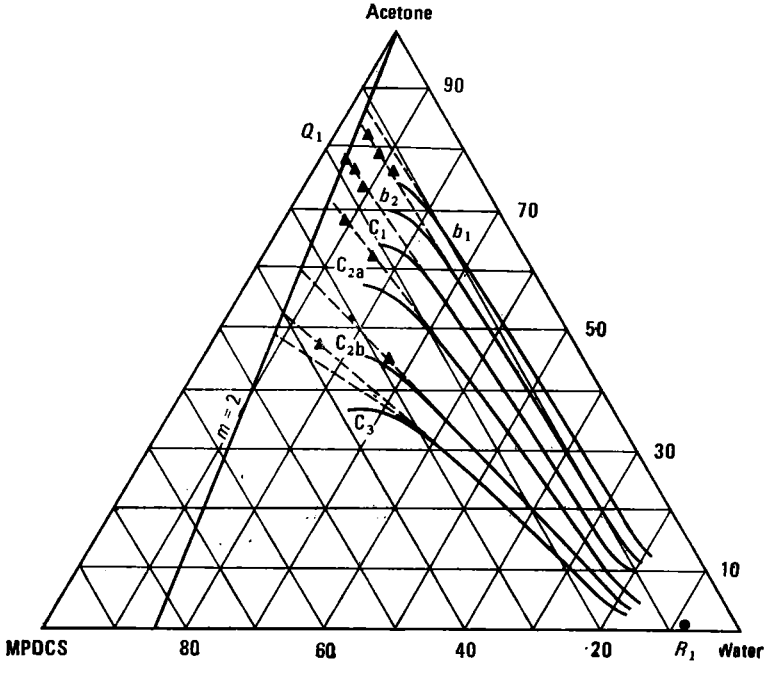


Fig. 12. Experimental nodes of phase equilibrium of the MPDCS-water-acetone reaction system (pH 7.8 to 8.0). Filled triangles stand for experimental evidence without acceptor HCl (pH < 1)

tion, however, should not significantly affect the composition of HP products.

Shown in Fig. 13 is the relationship between the amount of D_4 formed in the aqueous phase and the amount of α,ω-dihydroxysiloxanes in the chlorosilane phase as a function of the phase mass ratio.

Since during the hydrolysis of MPDCS, oligosiloxanes are formed due to a shortage of water in the "chlorosilane" phase, and D_4 is formed in the aqueous phase, a change in the mass ratio of the phases will alter the relative amounts of the products referred to [30, 31].

The phase state of the MPDCS-water-acetone reaction system just discussed is a simplified approximation. The first acts of interaction involving silane and water yield methylphenylchlorohydroxysilane, and the reaction system becomes a four-component one. A tentative consideration of the latter has shown that a fan-shaped pattern of

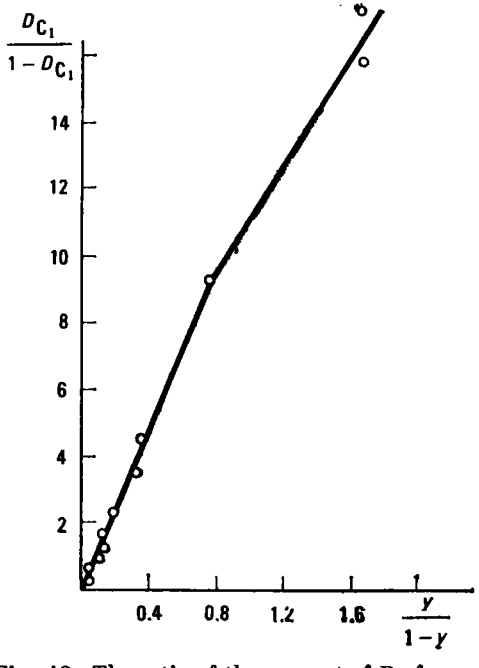


Fig. 13. The ratio of the amount of D_1 formed in the aqueous phase to the amount of siloxanes in the chlorosilane phase versus the phase ratio (y is the mass of the aqueous phase)

nodes corresponds to the reaction-phase surface of the heterogeneous system of the second type, namely, MPDCS-(methylphenylchlorohydroxysilane + acetone)-water.

The foregoing suggests that control of the phase state of reaction system is helpful in directing the hydrolytic polycondensation of organosilicon monomers so as to produce predominantly specific homologues. The HP of organotrichlorosilanes is a more complex process, notably, that of methyltrichlorosilane (MTCS) which has the greatest practical utility and whose HP was investigated by Andrianov and co-workers [13-18]. The phase state of the reaction system in the case of the MTCS HP is characterized by solubility of the hydrolysis starting products in water and the need to use organic solvent for their extraction.

In view of the complex composition of the products resulting from the MTCS HP, the amount of the gel thus formed and the gelatinization time of soluble oligomers are employed as the key criteria for

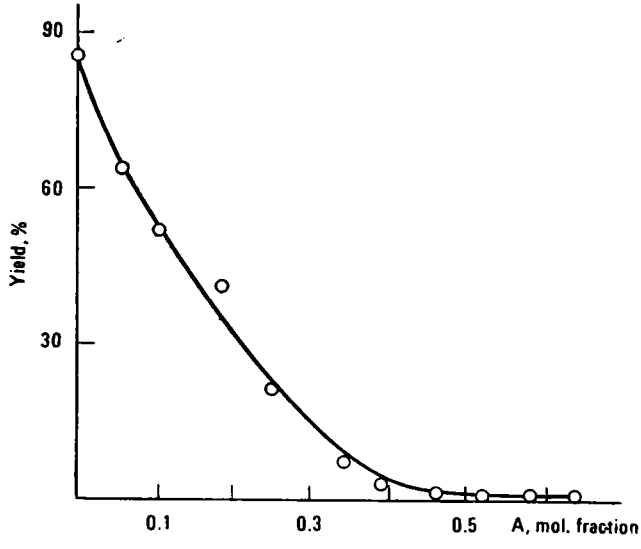


Fig. 14. The yield of gel following the HP of methyltrichlorosilane as a function of the acetone content in its mixture with toluene [13]

evaluating the extent of the process involved. As illustrated in Fig. 14 [13], a rapid drop in the amount of a three-dimensional product with increasing portion of acetone in its mixture with toluene may serve as a confirmation of the transition of the process from the heterogeneous to the homogeneous region and of a reduction in the relative proportion of the heterofunctional polycondensatoin process.

2.4. Formally Kinetic Analysis of Hydrolytic Polycondensation

Analysis of the hitherto accumulated data concerning the effects of the amount and species of solvent [13, 34], pH media [35], temperature [14], and the order of introduction of reactants [34, 36] on the yield of soluble oligoorganosilsesquioxanes resulting from HP suggests that if they are to be produced in meltable and soluble forms, it is necessary to intensify the process of hydrolysis, that is, to increase the amount of water in the reaction zone, and to reduce its amount if the losses of the water-soluble starting products of the hydrolysis are to be cut.

In the case of the MTCS HP it was possible to settle this contradiction by using water-salt solutions as a hydrolyzing agent and carrying out the HP under the conditions of the reaction mixture being recycled [36, 37]. In view of the complex composition of the products yielded by the MTCS HP and difficulty encountered in their identification (especially at intermediate stages), to derive quantitative dependences of the process involved, use was made of a formally kinetic approach [38] underlied by the following assumptions:

(i) a system of two-phase pattern: an aqueous solution of HCl and a salt and an organic solution of oligomethylsilsesquioxane (OMSSO) formed upon hydrolysis;

(ii) a constant area of phase contact: in the organic phase under the action of HCl available in the aqueous phase, OMSSO undergoes further polycondensation whose rate was determined from the time taken by the organic phase to lose fluidity;

(iii) constant availability of the SiOH groups in all the starting OMSSO.

To describe OMSSO condensation, a kinetic model of the pseudohomogeneous katalytic reaction was chosen

$$\frac{1}{\tau}=B\cdot k_0[\mathrm{HCl}]^n\cdot\exp[B_1N_{\mathrm{H_2O}}+B_2N_s]\cdot(1+B_3[\mathrm{NaCl}]\cdot\exp\left(-\frac{E}{RT}\right) \qquad (9)$$

where τ is the gelatinization time (losses of fluidity by the solution OMSSO in an organic solvent); N_{H_2O} and N_s are the molar fractions of water and solvent, which characterize the composition of their mixture; k_0 is the OMSSO condensation rate constant; B, B_1, B_2, and B_3 are constants.

Research on the kinetics of the OMSSO heterophase condensation [39] under various conditions (contents of HCl, NaCl, acetone, and water) and analysis of experimental data using polynomial models have demonstrated that when these data presented as a function of electrometric pH they are well approximated by one function which, according to the concepts of acid-basic catalysis, is well linearized in corresponding coordinates (Fig. 15):

$$\ln k_{\mathrm{eff}}=-6.002-4.872\ \mathrm{pH},\quad r_f=0.998>r_{0.01}(23)=0.640 \qquad (10)$$

From this it is inferred that all the investigated factors regulate the activity of H_3O^+ ions in the aqueous phase; the activity of H_3O^+ ions controls the extent to which homofunctional condensation has been accomplished and, correspondingly, the structure of oligomer [39, 40].

When the same experimental findings are factored as a formal kinetics equation

$$k_{\mathrm{eff}}=7.559\times10^{-4}[\mathrm{HCl}]^{3.1}\cdot\exp(0.590\cdot\exp 0.560[\mathrm{NaCl}]) \qquad (11)$$

it will be seen that a third order for HCl and a "special catalytic effect" of sodium chloride are observed; the latter effect can be written as the following equation (Fig. 16):

$$\ln (y_1/y_1^c) = 0.162 z_4, \quad r_f = 0.995 > r_{0.0001}(6) = 0.963 \tag{12}$$

where y_1^c and y_1 are the time prior to the "gelatinization point" during the condensation of OMSSO with and without NaCl, respectively; and z_4 is the concentration of NaCl in the aqueous phase.

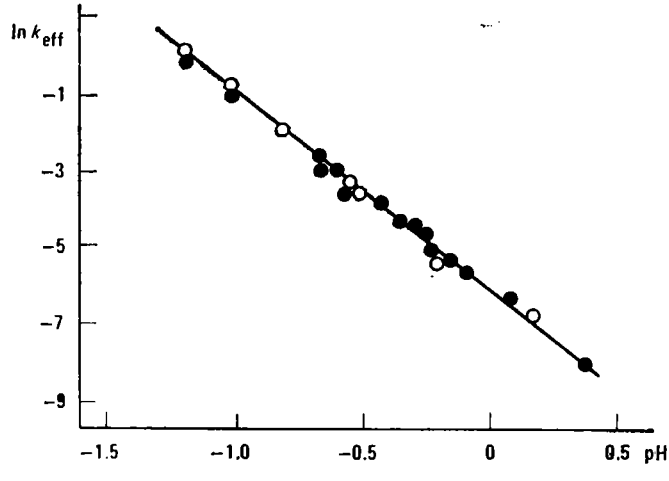


Fig. 15. Condensation rate effective constant of OMSSO solutions as a function of the electrometric pH of the lower phase (water-acetone-HCl).

Filled and open dots stand respectively for condensation with and without NaCl; a solid line signifies calculations by Eq. (10)

Effective use was made of the method of smoothing kinetic curves using multifactor models [37, 40, 41]:

$$\ln y_1 = 4.4561 - 1.7330 \cdot x_1 - 1.8171 \cdot x_1^3 + 1.6404 \cdot x_1^4 = 0.2102 \cdot x_2 - 0.5656 \cdot x_1 x_2 - 0.3957 \cdot x_2 x_3 \quad (R^2 = 99.69) \tag{13}$$

$$\mathrm{pH} = 1.660 - 1.010 \left(\frac{z_1 \cdot 100}{z_1 + z_2 + z_3} \right)^{1/3} - 0.0323 z_4 \quad (R^2 = 99.44) \tag{14}$$

where $x_1 = \frac{z_1 - 0.86}{0.76}$, $x_2 = \frac{z_2 - 2.85}{1.81}$, $x_3 = \frac{z_3 - 7.78}{4.00}$ and z_1, z_2, and z_3 are the specific consumptions of hydrogen chloride, acetone, and water, respectively, in g per g OMSSO.

Employment of models (13) and (14) and Eq. (15)

$$z_4^{2/3} = 4.13 - 1.98 \cdot x_1 - 0.75 \cdot x_2 + 1.43 \cdot x_3 \quad (R^2 = 93.79) \tag{15}$$

describing the dependence of the maximum concentration of NaCl on the same factors allows constructing a nomogram with a view to selecting conditions for the MTCS HP (Fig. 17).

From the above discussion it is clear that depending on the conditions of HP the resulting OMSSO may vary in structure and, as a consequence, will differ in properties. One of these properties is thermal and thermooxidation stability of polymethylsilsesquioxanes

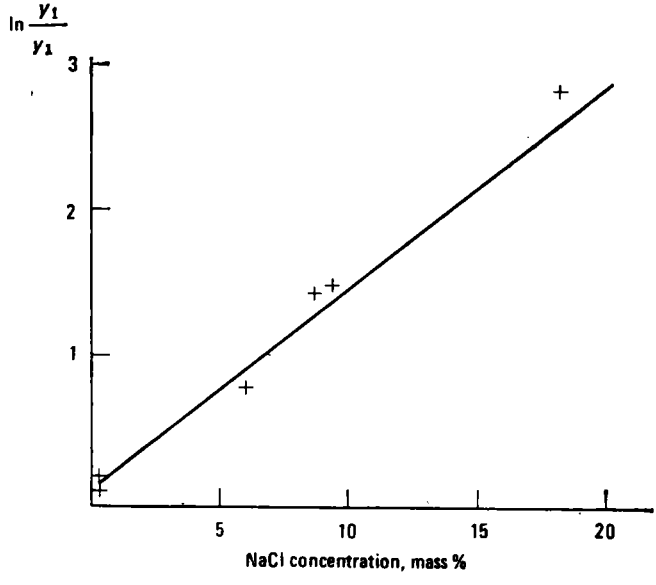


Fig. 16. Relative rate of OMSSO condensation versus NaCl concentration in the aqueous phase

(PMSSO) resulting from OMSSO. Referring to Fig. 18, on synthesis of starting oligomers, HP will greatly affect the value of mass losses when heating PMSSO.

The employment of small amounts of chlorides of other metals chosen from groups of effective thermostabilizers in the synthesis of OMSSO by the hydrolytic polycondensation of MTCS other than NaCl permits varying the dimensions of the starting cyclic blanks in OMSSO and considerably altering thermal stability of the resulting PMSSO [42]. In this case thermal stability proved interrelated to the nature of the cation and the order of its introduction into HP.

In addition to thermal characteristics, the structural features of oligomethylsilsesquioxanes and their polymers also manifest themselves in IR spectra [43]; specifically, there were detected two types of CH_3 substituents to which a doublet of pendular oscillations

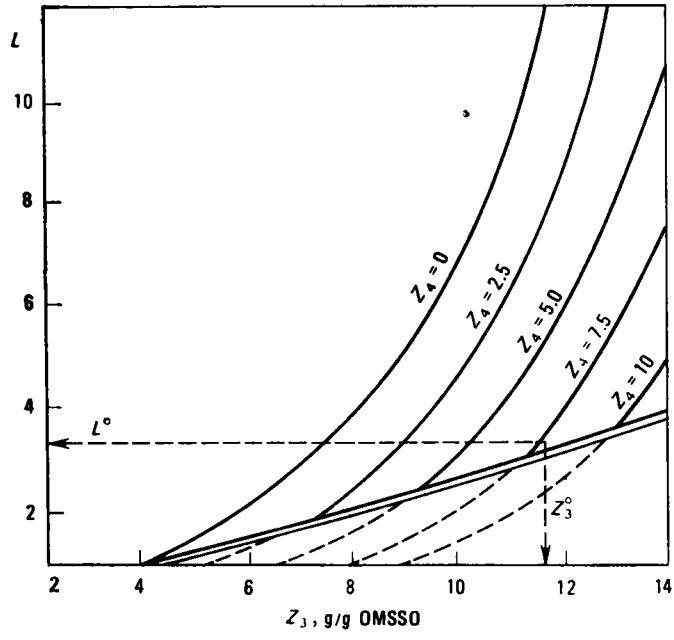


Fig. 17. Relative rate of OMSSO condensation (L) versus specific water consumption (z_3) for constant levels of HCl (z_1=1.630 g/g OMSSO), acetone (z_2=2.588 g/g), and at varying concentrations of NaCl (z_4, mass %).

The double curve stands for an isoline for homogeneous solutions

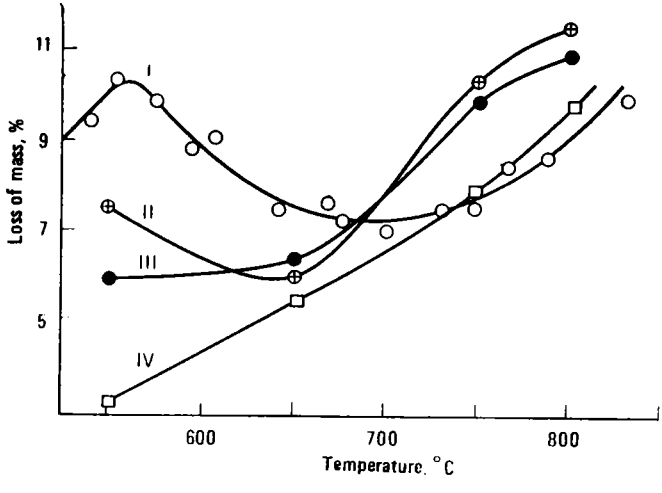


Fig. 18. Thermooxidative degradation of polymethylsilsesquioxanes obtained by curing OMSSO. Starting oligomers are synthesized by hydrolytic polycondensation of methyltrichlorosilane: I — without solvent, II-IV— in the acetone-toluene-water system at 55 °C (II), 29 °C (III), and 0 °C (IV)

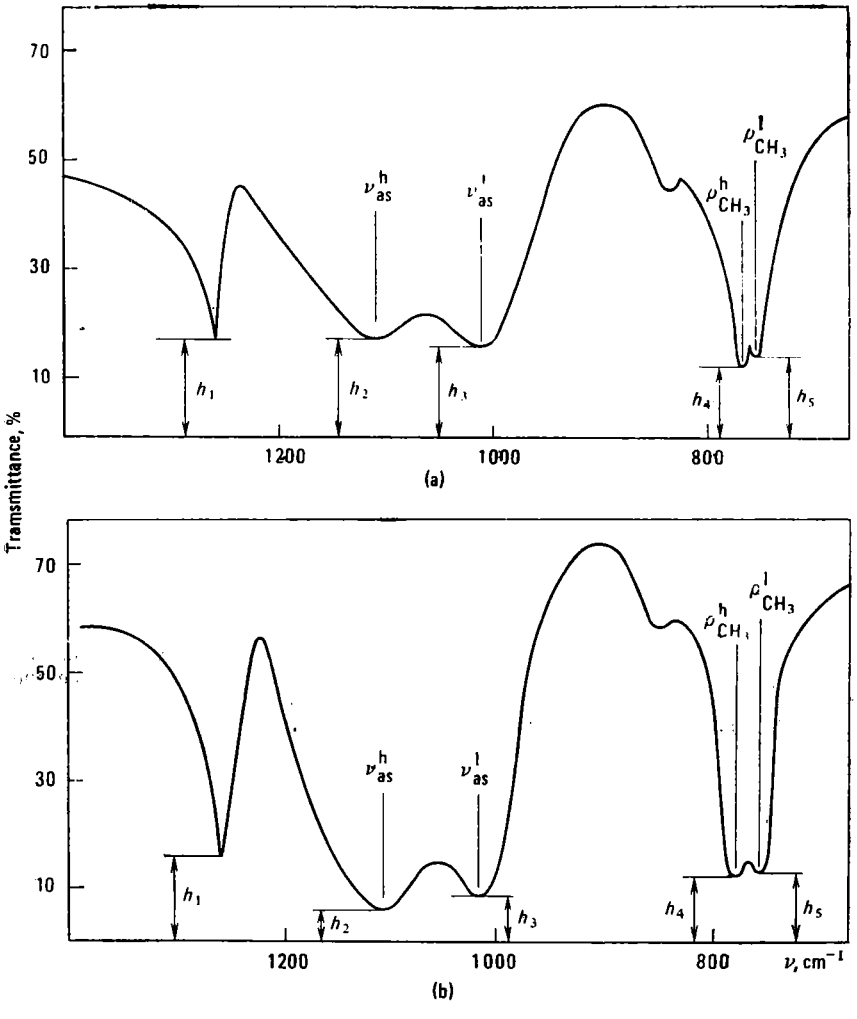


Fig. 19. IR spectra of polymethylsilsesquioxanes on the basis of oligomers synthesized in the presence of $ZnCl_2$ (*a*) and $FeCl_3$ (*b*)

ρ_{CH_3} corresponds in the region from 762 to 780 cm^{-1} (Fig. 19). A statistically effective model was brought out to relate PMSSO mass losses (ΔW) to the characteristics of IR spectra:

$$\Delta W = 208.59 - 0.6436\rho^{high}_{CH_3} + 0.3453\rho^{low}_{CH} + 34.42\,(h_2/h_1)^{0.25} - 3.792\,(h_3/h_1) \quad (R^2 = 98.83) \qquad (16)$$

Analysis of the equation suggests that the thermal stability of PMSSO is the higher, the greater the difference in the position of CH_3 radicals in PMSSO structural fragments; the greater the transmission ratio between the low- (ν_{as}^{low}) and high-frequency (ν_{as}^{high}) components of the band of stretching vibrations of the SiOSi bond; the greater the intensity of deformation vibrations of the CH_3 groups.

Analysis of the facts indicates that the position ν_{as} of the SiOSi bond is governed by its electronic structure which in turn depends on the nature of the substituents, length and conformation state of the adjacent parts of the chains playing the part of unusual substituents. The latter is well illustrated by the shift ν_{as} of the SiOSi bond in disiloxanes and cyclotetrasiloxanes (Table 2). Indeed, if the characteristics of the fragment —$OSi(R)_2OSi(R)_2O$— acting as a substituent in the SiOSi bond are supposed to vary only slightly with R, the effects produced by substituents CH_3 and H in the compounds involved must be similar, which is supported by the data listed in Table 2.

Table 2. Shift in position ν_{as} in a successive substitution of H for CH_3 groups in the SiOSi bond

Compound	$\Delta\nu_{as}$ (cm^{-1}) at the values of n					
	1	2	3	4	5	6
Disiloxanes $H_n(CH_3)_{6-n}Si_2O$	3.4	9.6	17.7	27.2	38.1	50.0
Cyclotetrasiloxanes $[H_n(CH_3)_{8-n}Si_4O_4]$	6.8	12.5	22.7	34.3	—	—

The extent of the effects of the mass, the number of H atoms, induction and steric constant substituents on the position ν_{as} of the SiOSi bond for the case of disiloxanes was quantitatively estimated [43]. In the factor space studied, the position of the given band proved to be 93.7 per cent dependent on the electronegativity of the substituents and merely 5.7 per cent on their mass. This evidence corroborates the assumption that the structure of PMSSO is interrelated with the polarity of the SiOSi and SiC bonds. This is reflected in the altered ratios of ν_{as} intensities of the SiOSi bond and ρ_{CH_3}.

The afore-discussed interrelations between the phase state of the reaction system during HP, the ratio and rate of introduction of starting components, and specific structures of the resulting OMSSO and polymers formed on their basis have made it possible to carry out their directed synthesis and obtain binders with improved techno-

logical indices. Composite materials produced on the basis of such binders exhibit better physicomechanical properties alongside greater thermal stability [44].

3. SYNTHESIS OF POLYMERS BY POLYMERIZING CYCLIC SILOXANES

Recent years have seen considerable advances in the field of synthesizing polyorganosiloxanes by polymerization of cyclic oligomers; specifically, novel basic patterns have been elucidated in the kinetics and mechanism of polymerization of cycles in the presence of various types of catalysts and catalytic systems.

It has become common use to consider that with alkali metals polymerization of organocyclosiloxanes and organocyclocarbosiloxanes is first order relative to monomer and 0.5 with respect to catalyst, with the latter increasing to unity on introduction of polar additives [45]. Since silanols were found to exhibit a great tendency towards association [46], it was presumed that the catalyst is available in the reactive mixture in the form of associates and the order relative to it is defined by the rate of dissociation into active ion pairs. This assumption is currently considered to have become common use [47]. The activity of such catalysts, that is, the rate of their dissociation, can be enhanced via introduction of polar substances capable of solvating the cation and facilitating separation of the ion pair.

3.1. Polymerization of Organocyclosiloxanes by Silanolates and Silanols

Research on the polymerization of hexamethylcyclotrisiloxane (D_3) under the action of sodium trimethylsilanolate (STMS) has demonstrated that it is non-equilibrium (higher cycles are missing in products) and that it is first order with reference to monomer and catalyst [48]. The first order with respect to catalyst was ascribed to the reaction proceeding on the surface of the associates when the average degree of association is not sensitive to changes in its concentration, and the number of active sites is proportional to the overall concentration of the catalyst [49].

Reaction of STMS with trimethylsilanol modelling the silanol end of the growing chain has separated several STMS crystal hydrates which, according to X-ray diffraction analysis, have layer structure [50] whereas the isolated STMS crystals (synthesized by the reaction involving Me_3SiOH and Na in toluene) are the associates of spherical structure and composition $(Me_3SiONa)_{10}\cdot NaOH$ [51]. The reaction between the latter and trimethylsilanol (TMS) yields less stable and more active associates of layer structure.

When mixtures of STMS and TMS were used as catalysts on polymerization of D_3, the first order with respect to monomer was also observed. As the TMS to STMS molar ratio (α) increases in the range 0-15, the reaction rate constant increases 30-plus times, with the least pronounced change occurring over the range $\alpha=0$-2 and with the most pronounced change, at $\alpha=2$-5 [52]. This can be attributed to the breakdown of the self-associates of STMS and dimethylsiloxanolate groups due to complexing with TMS and end silanolate groups newly emergent from polymerization—the destruction of associates is equivalent to an increase in the effective concentration of catalyst. Rapid proton-cation exchange whose presence has been borne out by ^{1}H NMR [53] and ^{13}C NMR [54] spectroscopy is presumed to be a driving force for destroying associates. It has also been found that the entropy term is predominantly changed on the formation of a transition state with growing α, and the potential barrier is thus lowered and the catalyst's activity is enhanced [55, 56].

A similar picture is observed when alcohols are introduced as alternatives to TMS, namely, enhanced activity of the catalyst on account of the destruction of its associates due to complexing with alcohols and silanol groups yielded by copolymerization [57, 58].

The rate of the copolymerization of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane (A_3) and diethylene glycol (DEG) in the presence of KO [(Me)(Ph) SiO]$_3$K under the conditions that make the formation of water impossible is given by the equation $w=k[A_3][SiOK]_0$, that is it is independent of the glycol concentration. Analysis of potential reaction schemes has indicated that the consumption of DEG in the kinetic portion is associated with proton-cation exchange which occurs between DEG and the catalyst and subsequent interaction between alcoholate and cyclosiloxane [58].

The same reaction run in boiling toluene in the presence of KOH is accompanied by condensation of silanol groups and formation of water. The rate of water formation depends on the ratio $q=(A_3/DEG)$: up to 50-60% conversion it obeys a second-order equation, it reaches its maximum when $q=2$-4, and it is independent of the catalyst concentration. Similar regularities are also observed in the copolymerization of DEG with D_3 and D_4.

3.2. Polymerization of Organocyclosiloxanes with Tetraorganoammonium Catalysts

Onium compounds are extensively used as highly effective catalysts for polymerization of organocyclosiloxanes and for silanol condensation. To illustrate, the following order of activity of onium catalysts for polymerization of D_4 was established [47]:

$Bu_4NOH > Bu_4AsOH > Me_4NOH > Me_4SbOH > Me_3SOH$

For a quantitative study of the factors influencing thermal stability, catalytic activity, and interaction with proton donors, use was made of α,ω-bis(tetraorganoammonium)oligodimethylsiloxanolates $R_4NO(Me_2SiO)_nNR_4$, where R_4=Me_4, Et_4, Bu_4, Me_3Ph, $Me_3(PhCH_2)$, $Me_2(Ph)(Et)$, $Me_2(Ph)(Bu)$, which had been synthesized via reaction of D_3 with aqueous solutions of corresponding ammonium bases [59].

An investigation of the polymerization kinetics of D_3 in the presence of tetramethylammonium bis-silanolate has revealed that the

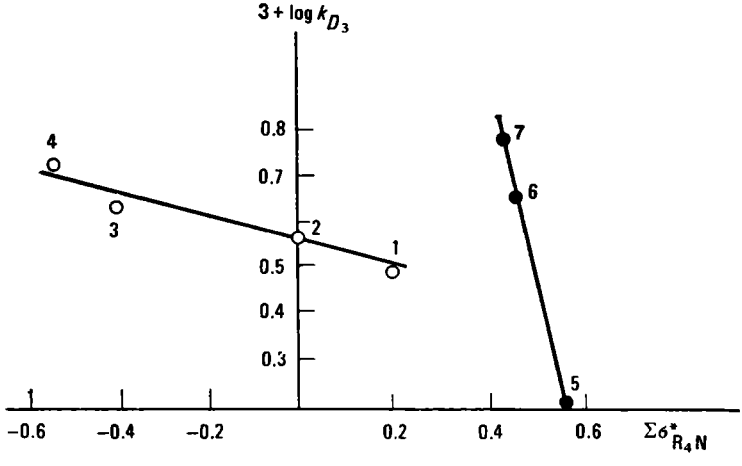


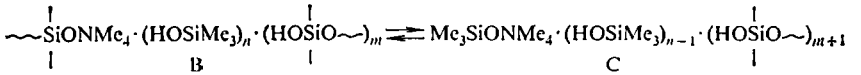
Fig. 20. Rate constants of D_3 polymerization versus induction constants of substituents in nitrogen in $R_4NO[Si(Me)_2O]_nNR_4$

M_4 values: *1*—Me_3PhCH_2, *2*—Me_4, *3*—Et_4, *4*—Bu_4, *5*—Me_3Ph, *6*—$Me_2(Et)(Ph)$, *7*—$Me_2(Bu)(Ph)$

reaction is first order with respect to monomer, and first order with respect to catalyst. Depending on the nature of an organic radical, bis-silanolates can be classified into two groups [60]: the first group comprises compounds containing no C-aryl bond while the second group encompasses species containing such a bond. In both groups reactivity increases with increasing electron-donor capacity in nitrogen substituents: for each group of the substituents, the value of log k_{D_3} varies linearly with $\Sigma\sigma^*$ (Fig. 20) whereas the constant of the reaction series ρ is negative, which indicates the nucleophilic nature of the reaction between the catalyst and D_3 while the absence of higher cycles in the reaction mixture is testimony to the occurrence of a non-equilibrium process [60, 61].

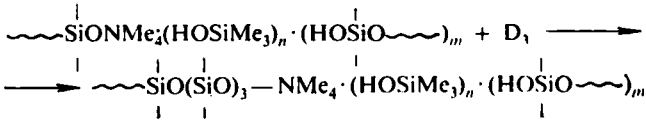
As in the case of polymerization under the action of silanolates and alkali metals, when tetraorganoammonium bis-silanolates are employed their activity is affected by addition of proton donors, TMS

[48, 62], water [63], and alcohols [64]. Unlike the STMS+TMS system, the presence of an additive of trimethylsilanol lowers the rate of polymerization. It is believed [48, 62] that due to proton-cation exchange equilibrium is reached in the TMS-bis-silanolate system:



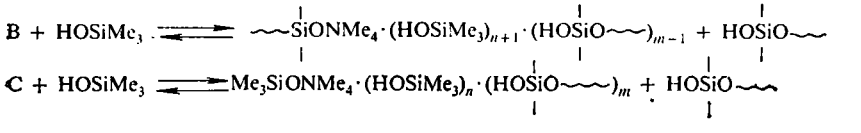
(17)

The polymerization reaction is of a complex nature; its decisive stages involve the reaction of D_3 and TMS with complexes B and C, with no direct reaction between D_3 and TMS. The reaction between D_3 and complex B (or C) results in the growth of a siloxane chain (homopolymerization) [63]:



(18)

The reaction of trimethylsilanol with complexes B and C displaces, as it were, siloxanol and introduces a novel TMS molecule into the complex:



Thus, the reaction of D_3 with complex C and a subsequent exchange occurring in complex B thus formed (17) result in an irreversible conversion of TMS according to the following equation:

$$Me_3SiOH + (Me_2SiO)_3 \rightarrow Me_3SiO(Me_2SiO)_3H$$

that is, the copolymerization of D_3 and TMS is observed.

Research on the effects of water additives on polymerization of A_3 and D_4 [63] has demonstrated that the process of interest incorporates a stage at which water complexes of low activity with a terminal silanolate group are formed; the complexes involved react with organocyclosiloxane to give chains with end groups. Molecules with silanol and silanolate groups at their ends grow at equal rates, since due to proton-cation exchange the siloxanols become active periodically, the exchange rate considerably exceeding that of poly-

merization. This conclusion is in agreement with evidence from the work [65] where a study was made into polymerization of D_3 in the presence of water and bis(pyrocatechinoxy)phenylsiloxanolate of trimethylbenzene ammonium, and the interrelationship between the number of growing chains and the amount of water in the reaction mass as well as a linear dependence of polymer's molecular weight on the conversion of D_3 were demonstrated.

Due to their lower acidity, aliphatic alcohols exert weaker effects upon the rate and composition of the products of D_3 polymerization [64]. This is responsible for the weakening of their ability to form complexes with catalyst and the shifting of proton-cation exchange between the alcohol and siloxanolate towards the latter. For instance, with propyl and butyl alcohols, the D_3 polymerization rate constants become one-third of their values in the process involving no alcohol additive, whereas the reduction is 20-fold in the presence of TMS under the same conditions.

3.3. Polymerization of Cyclosiloxanes in the Presence of Amines

As compared with alkali metals or onium compounds, amines are less active non-ionic nucleophilic catalysts to polymerize organocyclosiloxanes. Amines are presumed to form an intermediate with organocyclosiloxane, with the SiO bond of the ring being split

to produce the $R_3N^+\overset{|}{Si}O\sim\sim\overset{|}{Si}O^-$ zwitter-ion responsible for the further growth of the chain.

In the presence of water, alcohols, or silanols, the reaction of interest proceeds in milder conditions because quaternary ammonium base is formed [66]:

$$R_3N + H_2O \rightleftharpoons \overset{+}{H}NR_3OH^- \xrightarrow{\geqslant SiOSi\leqslant} \overset{+}{H}NR_3O\overset{|}{Si}O\sim\sim\overset{|}{Si}OH$$

In the presence of piperidine and its equimolar mixture with water in sealed ampoules at 130 °C, the polymerization of A_3 exhibits first order with respect to monomer; with respect to piperidine the reaction is also first order if no use is made of additives. With water, however, the reaction becomes second order, and the rate of polymerization is also substantially increased [67]. Alcohol additives produce similar effects, too; utilization of polyglycols has enabled carboorganosiloxane copolymers to be synthesized. Copolymerization of A_3 with polyethylene glycol in the presence of Et_3N will not pro-

ceed, but introduction of 5-10% water leads to the formation of products similar to those yielded in the presence of $KO[Si(Me)(Ph)O_3]K$. Copolymerization of A_3 with oligophenolphthaleinophthalate takes place in the presence of pyridine in boiling dioxane with a subsequent completion of the process following distillation of the solvent at 150 °C and a drop in the pressure [67].

3.4. Catalysis of Reactions of Formation and Cleavage of Bonds by Ionic Fluorides

Due to the high affinity of the F^- ion to silicon, ionic fluorides exhibit high catalytic activity in the transesterification of alkoxysilanes by alcohols [68], in the cleavage of the SiO bond [69-72], in the hydrolysis reactions of organoxysilanes [73-75], on the dehydrocondensation of alcohols with organohydride silanes [76-79], and on a catalytic reduction of aldehydes with organohydride silanes [77, 79]. Research on the reaction of diphenylmethylsilane with various alcohols in the presence of Me_4NF has revealed that the reaction is first order with respect to silane, zero order with respect to alcohol, and second order with respect to the catalyst, which drastically differs from the action of catalysts of alkaline type. The reaction rate constants correlate with the values of the substituents' induction constants with allowance made for the steric effect; here, the positive value of the constant of the reaction series ρ indicates the electrophilic nature of the process.

Heating of 1,3-dihydrotetramethyldisiloxane in the presence of Me_4NF or Bu_4NF has revealed that a disproportionation reaction occurs so that hydride hydrogen will be transferred from one silicon to another and dimethylsilane will be eliminated [82]. Up to 50% of azobenzene as well as hexaphenylcyclotri- and octaphenylcyclotetrasiloxanes were isolated as products from reduction of nitrobenzene by diphenylsilane [83].

Ionic fluorides are effective catalysts for the polymerization of organocyclosiloxanes, the catalyst's activity being a function of the nucleophilicity of fluoride [84-86]. For example, Me_4NF and Bu_4NF polymerize D_4 and A_3 whereas KF and CsF, without polar additives, bring about polymerization in A_3 only. The polymerization of D_4 in the presence of Me_4NF is of an equilibrium nature, the process being characterized by the availability of an induction period, first order with respect to monomer and second order with respect to catalyst. The polymerization of D_3 in the presence of Me_4NF and TMS [86] exhibits the enhanced activity of the fluoride. In this case, an increase in the amount of silanol causes a decrease in the magnitude of the induction period on whose completion the reaction is first order with respect to monomer. The increased polymerization rate can be attrib-

uted to the reaction between Me_4NF and Me_3SiOH yielding hydroxides and then tetramethylammonium silanolate which conducts the polymerization [84-86].

3.5. Vulcanization of Organosilicon Rubbers

Alongside chemical and physicomechanical methods of exploring vulcanization processes of organosilicon rubbers by end groups, viscosimetry [87] and spectroscopy of products yielded by the reaction involving model substances [88, 89] have recently been

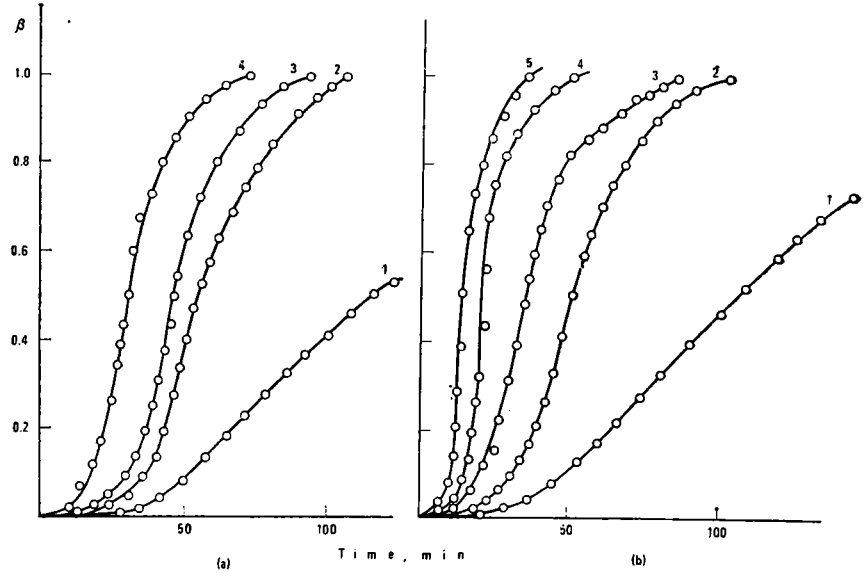


Fig. 21. Variations of β in the process of curing organosilicon rubbers СКТН-Г (*a*) and СКТВ-С (*b*) [92]

Temperature, °C: *a*: *1*—20, *2*—50, *3*—60, *4*—80. *b*: *1*—20, *2*—50, *3*—60, *4*—70, *5*—90. Curing agent—4 mass % of tetraethoxysilane with respect to rubber

employed for this purpose. More comprehensive data concerning the cross-linking of organosilicon rubbers, notably low molecular weight species, can be advantageously derived by a rheokinetic technique, which notes alterations in the dynamic modulus of elasticity G during the vulcanization process [90, 91].

On the basis of changes occurring in G in two types of organosilicon rubbers (Fig. 21), it was proposed [90] to describe their vulcanization process occurring in isothermal conditions using the follow-

ing equation:

$$\dot{\beta} = k(1-\beta)(1+C\beta)$$

where β is the conversion level: $\beta = \frac{G-G_0}{G_\infty - G_0}$; G, G_0, and G_∞ are the current, initial, and final values of the dynamic modulus on vulcanization, respectively; k is the reaction initial rate constant (when $\beta \to 0$); and C is the constant characterizing an increase in k with increasing conversion.

The values of constants k and C have been found graphically from the time dependence of $\ln[\beta/(1-\beta)]$, these quantities being in reason-

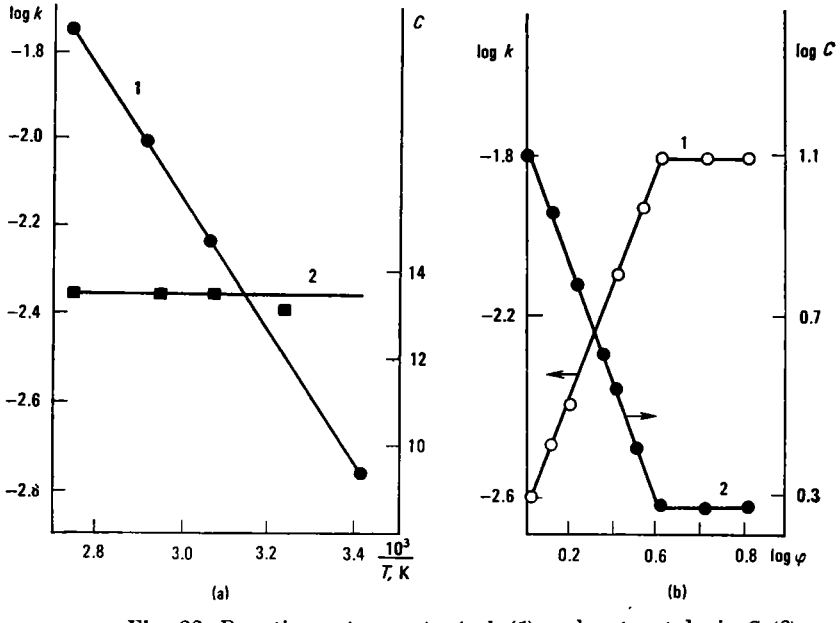


Fig. 22. Reaction rate constants k (*1*) and autocatalysis C (*2*) versus inverse temperature (*a*) and the logarithm of the amount of the curing agent φ (*b*)

a—CKTH-Г, 4 mass % TES with respect to rubber; *b*—CKTB-C, 80° C

ably good agreement when measured both by the rheokinetic method and gel-sol analysis [91]. For instance, when rubber CKTH-Г is vulcanized by 4 mass % tetraethoxysilane in the presence of 1% tin dioctoate at 20 °C, k equals 1.1×10^{-3} and 0.85×10^{-3} min^{-1} (respectively, when determined by the rheokinetic method and swelling), while the value of constant C is the same ($C=12.2$).

Constants k and C give the macrokinetics of cross-linking, their values varying inversely with an increase in the content in the curing agent system (Fig. 22). Constant C does not change with tempera-

ture, and the vulcanization activation energy of the low molecular weight α,ω-dihydroxydimethylsiloxane rubber, derived from the temperature dependence of k, is 23 kJ/mole (Fig. 22), which is much lower than E_a for a similar system of model substances [88, 92].

The proposed macrokinetic description of the vulcanization of organosilicon rubbers is also applicable when the vulcanization mechanism is not known.

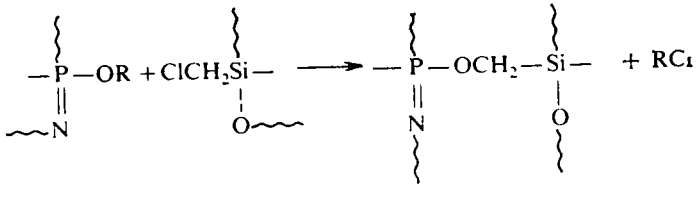
A study of the molecular parameters of the polydimethylsiloxane network on the basis of the cold-vulcanized rubber CKTH-Γ has shown [91] that the average value of $M_c = (2.2 \pm 0.2) \times 10^4$ is smaller than the one predicted by high-elasticity theory [93] which states that M_c must equal the average molecular weight of rubber prior to vulcanization. Presumably, the branchings available in industrial rubber CKTH-Γ reduce the length of the chain parts between the cross-links. At the same time the value of M_c derived in the study referred to above [91] is smaller than the one established for polydimethylsiloxane-based gels [94].

4. PHOSPHAZENE-CONTAINING ORGANOSILICON OLIGOMERS AND POLYMERS

To prosecute research on the synthesis of siliconphosphazene-containing polymers on the basis of chloromethylsilanes and chloromethylsiloxanes [95-97], the surface of silica gel has been modified by successive treatment with chloromethyldichlorosilane and alkoxyphosphazene [98]. In this case the use of partially substituted alkoxychlorophosphazene and a further hydrolysis of chlorine would give silica gel with oxyphosphazene groups capable of ion exchange.

The second option whereby similar sorbents can be produced involves a hydrolytic copolycondensation of chloromethyltrichlorosilane with other chlorosilanes to form chloromethyl-containing gel attended by its treatment with linear or cyclic alkoxyphosphazenes [99].

The reaction between polyorganosiloxanes containing chloromethyl groups at chain ends or as lateral substituents and polydialkoxyphosphazenes (alkoxy group OEt or OBu-*n*) has synthesized several graft or block copolymers [100-102]. In some instances the macromolecular reaction



is characterized by the low completion of the processes with respect to alkyl chloride and the discrepancy between its amount and the yield of gel fraction [102]. Despite the fact that the reaction exhibited a considerable degree of completion with respect to alkyl chloride the use of oligomeric polydimethylsiloxanes with terminal chloromethyl groups with a view to vulcanizing polydiethoxy- and polydibutoxyphosphazenes did not produce a cross-linked polymer, which pointed to a predominant grafting of siloxane chains to phosphazene ones. Only in the case of polysiloxanes featuring a considerable content of chloromethyl groups cross-linked polymers were formed; some characteristics are listed in Table 3.

Table 3. Some Characteristics of Polyphosphazenesiloxanes [102]

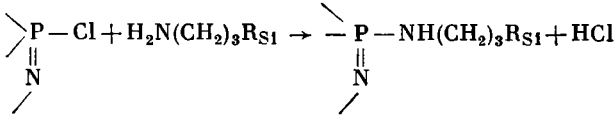
Content of $ClCH_2$ groups in siloxane, mass %	Siloxane to phosphazene weight ratio	Copolymer density at 20 °C, g/cm³	Huggins constant (dioxane, 30 °C)	M_c
Polydibutoxyphosphazene with $\eta = 0.60$ *dl/g (benzene, 25 °C)*				
14.1	0.5 : 1	1.064	0.96	800
5.4	1 : 1	1.059	0.70	300
45.6*	0.4 : 1	1.084	0.92	400
8.7	1 : 1	1.075	0.81	13 000
Polydiethoxyphosphazene with $\eta = 0.45$ *dl/g (ethanol, 20 °C)*				
5.4	1 : 1	1.071	0.65	300
14.1	3 : 1	1.091	0.78	400
8.7	2 : 1	1.088	0.76	900

* Polychloromethylmethylsiloxane.

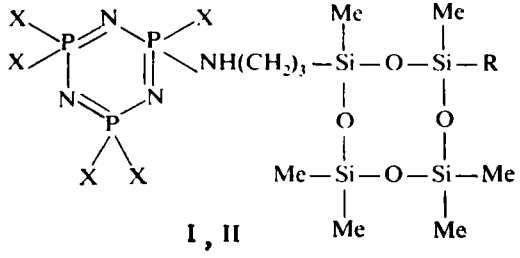
According to the data of thermomechanical analysis, the glass-transition temperature of polysiloxanebutoxyphosphazenes ranges from —90 to —80 °C, and for polysiloxaneethoxyphosphazenes, the range is from —60 to —40 °C, depending on the ratio of siloxane to phosphazene fragments. Copolymers preserve the abitity to undergo high-elastic deformation up to 180-200 °C; it is worthy of note that the latter is accompanied by 10-15% non-reversible deformation which is due to the microgel structure of copolymers and the availability of interstructural siloxane "grease" [102].

An alternative, recently developed route to synthesize phosphazene-containing polysiloxanes makes use of carbofunctional organo-

silicon amines:



For the reaction with hexachlorocyclotriphosphazene, use was made [103] of specially synthesized 3-aminopropylmethylsiloxanes, say, $H_2N(CH_2)_3Si(Me)[OSi(Me)_3]_2$ or tetracyclosiloxane compounds containing from 1 to 4 aminopropyl groups (other substituents were Me, H, or ethoxy groups). The scheme referred to was utilized to synthesize several novel silicon-containing phosphazenes, including compounds that follow [104]:



I, II

where X=Cl, NHMe or NMe_2; R=Me or H; I : X=Me_2N, R=Me; II : X=NHMe, R=Me.

Compounds I and II are readily formed at 20 °C in benzene in the presence of Et_3N, and amine can be replaced by its trimethylsilyl derivative. In this case trimethylchlorosilane is isolated instead of HCl, and the reaction proceeds at elevated temperatures.

Substitution of methyl- and dimethylamine radicals for chlorine atoms in bicyclic compounds (X=Cl) takes place in THF at 20 °C in quantitative yields.

X-Ray diffraction analysis has identified the molecular and crystalline structure of compound I [105]. It was found that there is no direct interaction between the two rings; the flat phosphazene ring produces no tangible effect on the structure of the siloxane ring except for conformation (in octamethylcyclotetrasiloxane the ring conformation C-LC, and in the bicycle of I—B), while the linear chain linking the phosphazene and siloxane rings is flat.

The recognized geometry of the bicycle suggests that the phosphazene fragment should not affect the activity of the siloxane ring in the polymerization reaction under the action of nucleophilic catalysts (with the exception of the steric factor).

The homopolymerization of bicycle of II and its copolymerization with D_4 or A_3 conducted in block at 100 °C for 2 hours in the presence of 0.005 mole per mole of the bicycle of α,ω-bis(tetramethylammo-

nium)dimethylsiloxanolate (TMAS):

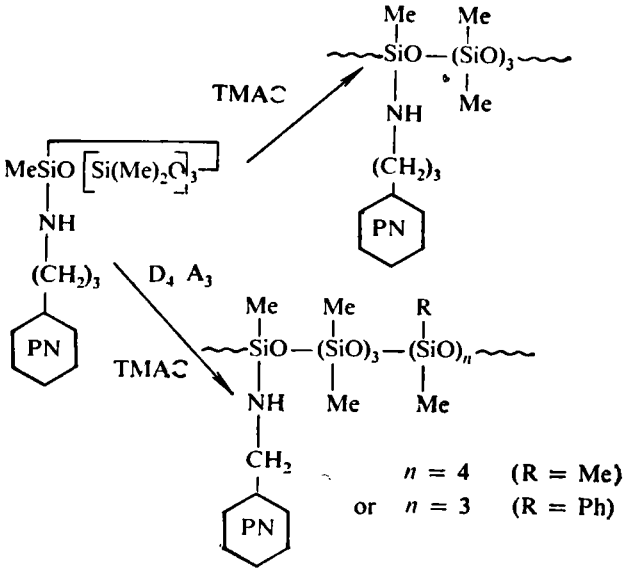


Table 4 illustrates that copolimerization proceeds more readily, whereas in contrast to polydimethylsiloxane, the resulting polymers are not soluble in toluene and hexane, which must be due to the presence of intermolecular hydrogen bonds between aminophosphazene side rings.

Table 4. Yield and Some Properties of Compound II-Based Polysiloxanephosphazenes

Initial monomers	Polymer, yield, %*	[η] dl/g (chloroform, 25 °C)	Softening temperature, °C	^{31}P NMR spectra (AX system)		
				δ_A, ppm	δ_X, ppm	J_{pp}, Hz
II	33	0.10	65	21.9	23.5	40.5
II+D_4 (1 : 2)	66	0.18	50	20.3	21.8	31.0
II+A_3 (1 : 2)	70	0.05	viscous fluid	22.1	23.2	31.0

* Following reprecipitation from a chloroform solution by toluene.

The fact that homo- and copolymers are formed by compounds of types I and II offers wide possibilities of modifying polysiloxanes by phosphazenes.

5. POLYORGANOSILAZANES

Most of the familiar polymeric organosilazanes exhibit the polycyclic structure of macromolecules with cyclic fragments being randomly arranged [21]. To prepare polymers that would contain cyclodisilazane and spirocyclic fragments as well as groups with nitrogen trisilylated atoms, several tetrafunctional amino silanes and organosilazanes have been synthesized and the processes of their thermal and thermocatalytic polycondensation have been investigated.

The reaction of aniline with dibromosilane gives bis(phenylamino) silane (III) in modest yield [106], while the principal product is 1,3-bis(phenylamino)-2-phenyldisilazane (IV):

$$H_2SiBr_2 + PhNH_2 \rightarrow \underset{III}{H_2Si(NHPh)_2} + \underset{IV}{PhN[(H_2)SiNHPh]_2} + PhNH_2 \cdot HBr$$

At the same time aniline reacts with diphenyldichlorosilane to yield predominantly $Ph_2Si(NHPh)_2$; here steric effects seem to hinder condensation. The coammonolysis of trimethylchlorosilane with diorganodichlorosilanes has synthesized the corresponding organosilazanes [107]:

$$R(R')SiCl_2 + Me_3SiCl \xrightarrow[-NH_4Cl]{NH_3} R(R')Si(NHSiMe_3)_2$$

where R=R'=Ph (V), R is vinyl, R'=Me (VI), R=H, and R'=Me (VII).

The yield of coammonolysis products depends on the nature of radicals and increases in the series $Ph_2SiCl_2 < (CH_2=CH)(Me)SiCl_2 < H(Me)SiCl_2$; the use of diphenyldichlorosilane was found to result in incomplete ammonolysis products containing the NH_2 group.

The composition of the products of $SiCl_4$ aminolysis by organic amines depends on the sizes of organic radicals in the amine and its basicity [108, 109]. For instance, the employment of excess amines with bulky substituents gives primarily tetrakis(organoamino)silanes:

$$SiCl_4 + 2RNH_2 \rightarrow Si(NHR)_4 + 4RNH_2 \cdot HCl$$

R=Et(VIII), R=*n*-Bu(IX), R=Ph(X)

The reaction of $SiCl_4$ with methylamine is made difficult by condensation processes. For example, in addition to $(MeNH)_4Si$ (XI), aminolysis with liquid CH_3NH_2 at −15 °C gives rise to 1,1,1,3,3,3-hexakis(methylamino)-2-methyldisilazane (XII) and 1,3,5-trimethyl-2,2,4,4,6,6-hexakis(methylamine)-cyclotrisilazane (XIII):

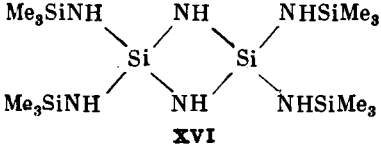
$$SiCl_4 + Me_2NH_2 \rightarrow \underset{XI}{(MeNH)_4Si} + \underset{XII}{MeN[Si(NHMe)_3]_2} + \underset{XIII}{[(MeNH)_2SiNMe]_3}$$

Amynolysis with gaseous methylamine (50 °C) primarily yields cyclotrisilazane XIII, which indicates prevalence of the condensa-

tion process arising both from elevated temperatures and lack of amine.

To prepare tetrakis(trimethylsilylamino)silane, the coammonolysis of $SiCl_4$ and Me_3SiCl was employed [110]. Only when a mixture of silanes is introduced into liquid ammonia does coammonolysis occur:

$$SiCl_4 + Me_3SiCl \xrightarrow[-NH_4Cl]{+NH_3} \underset{\textbf{XIV}}{(Me_3SiNH)_3SiNH_2} + \underset{\textbf{XV}}{(Me_3SiNH)_4Si} +$$

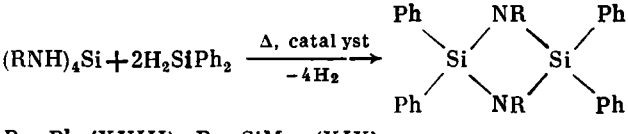


$$+ \underset{\textbf{XVII}}{[(Me_3SiNH)_2SiNH]_3}$$

XVI

The formation of cyclodisilazane (XVI) proved to be rather unexpected, since coammonolysis processes are most commonly accompanied by the formation of larger rings [21]. This is evidence that bulky trimethylsilyl groups have large effects upon the direction of condensation of intermediate products.

The reaction between silanes X and XV was investigated as a model for polymer synthesis [107]:



R = Ph (XVIII), R = $SiMe_3$ (XIX)

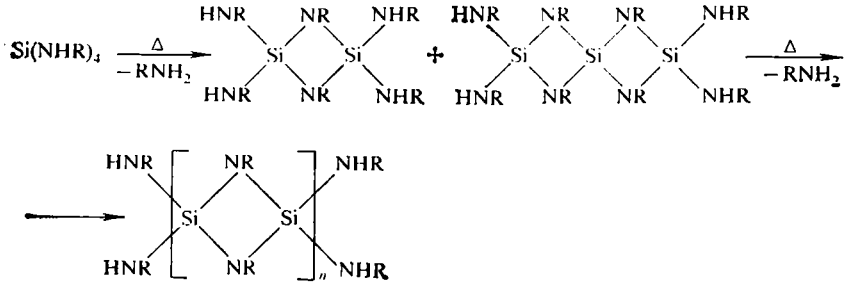
The formation of XVIII and XIX corroborates the fact that aminosilanes with bulky substituents are highly prone to give stressed spirocyclodisilazane structures and indicates that it is basically practicable to prepare polymers of this type.

The thermocatalytic condensation of V is accompanied by isolation of benzene [107]; consequently condensation that eliminates a phenyl radical is the principal process in this case. On 35% conversion (with respect to isolated benzene), a mixture of isomeric cyclodisilazanes was separated. 74% conversion gives an oligomer with the molecular weight up to 3000, which, on further condensation, loses solubility rapidly. The presence of cyclodisilazane fragments in the structure of the oligomer of interest was borne out by IR spectra.

The thermal condensation of compounds VIII and XI with a gradual rise in temperature up to 400 °C [108, 109] produces the corresponding cyclotrisilazanes in the initial stages; further heating is accompanied by an increase in the viscosity of reactive mixtures and fast structurization on 80% conversion with respect to the isolated

amine. Before the onset of gelatinization the molecular weights of oligomers range from 900 to 1000. In this case the network of the three-dimensional polymer is believed to be made of trisilazane rings [108, 109].

The condensation of compounds IX, X, and XV gives rise to oligomers that differ in the structure of the main unit:



where R=*n*-Bu (XXa, XXb), Ph (XXIa, XXIb), $SiMe_3$ (XXIIa, XXIIb).

30% conversion with respect to the amine isolated has given compounds XXa, XXb, XXIa, and XXIIIb in 16, 18, 19, and 17% yields, respectively. The thermal condensation of tetrakis(organoamine)silanes IX and X before 90% conversion is reached gives rise to soluble oligomers of spirocyclic four-membered structure with molecular weights about 2000. The condensation of tetrakis(trimethylsilyl)silane XV proceeds along similar lines [111]. In this case the reaction course is also borne out by isolation of intermediate products and their IR spectra. Defining the conformation and hydrodynamic characteristics of the polymer on the basis of XV has shown that its macromolecules feature enhanced rigidity.

Due to partial disproportionation, the thermal dehydrocondensation of 1,3-dihydro-1,3-dimethyl-1,3-diphenyldisilazane yields a linear polymer of the type ~~Si(Me)(Ph)N[Si(H)(Me)Ph]~~ alongside tris(methylphenylsilyl)amine [112].

X-Ray phase analysis was helpful in investigating thermal destruction of the XI-based polymer in nitrogen at temperatures ranging from 1200 to 1800 °C [113]. At temperature below 1400 °C the carbon residue is essentially an amorphous homogeneous mixture of carbide-nitride composition. From 1500 °C on crystallization starts and at 1800 °C it gives rise to a heterogeneous mixture of crystalline carbide and silicon nitride.

Research was continued on the synthesis of polyorganosilazosiloxanes which were prepared by polycondensation of oligosiloxanediols with aminosilazanes containing cyclosilazane structures [114], their combinations with linear silazane fragments [115], interaction of cyclotrisilazanes with α,ω-dichlorosiloxanes [116], and the copolymerization of D_4 and other cyclosiloxanes with diols containing a cyclodisilazane group [117]. The direction of these conversions depends on the ratio of starting substances, their nature, and temperature; depending on these factors silazane rings are liable to be kept, expanded, or split. In contrast to rigid-chain polyorganosilazanes with four-membered spirocyclic main units, their analogues with SiOSi bonds between silazane rings are related closer to polydimethylsiloxanes in conformation and hydrodynamic characteristics [118].

References

1. K.A. Andrianov, USSR Inventor's Certificate No. 55899, 1937.
2. K.A. Andrianov, *Zh. Obshch. Khimii*, 8, 1255 (1938).
3. J. Brown, *Khimiya i tekhnologiya polimerov*, No. 5, 3 (1965).
4. J.F. Brown, L.H. Vogt, and A. Katchman, *J. Amer. Chem. Soc.*, **82**, 6194 (1960).
5. J.F. Brown, *Rubb. Plast. Age*, No. 43, 877 (1962).
6. M.M. Sprung and G.O. Guenter, *J. Polymer. Sci.*, 28, No. 1, 17 (1958).
7. J.F. Brown, *J. Amer. Chem. Soc.*, No. 87, 4313-4316 (1965).
8. J.F. Brown, *J. Amer. Chem. Soc.*, No. 87, 4317-4320 (1965).
9. H. Gets and F. Massons, *J. Chem. Soc.*, A, 2682-2691 (1970).
10. B.R. Currell, H.F. Midgley, M.A. Seaborn, *et al.*, *Brit. Polymer*, 6, 229-240 (1974).
11. H. Inoue and S. Kohama, *J. Appl. Polymer Sci.*, 28, 2499-2508 (1983).
12. W. Ge and Y. Zhu, *Org. Chem.*, No. 2, 115-118 (1982).
13. K.A. Andrianov, T.V. Vasil'eva, B.I. D'yachenko, *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 1, 76-81 (1973).
14. K.A. Andrianov, T.V. Vasil'eva, and B.I. D'yachenko, *Zh. Obshch. Khimii*, 43, 768-774 (1973).
15. K.A. Andrianov, T.V. Vasil'eva, and B.I. D'yachenko, *Zh. Obshch. Khimii*, 43, 2458-2464 (1973).
16. K.A. Andrianov, T.V. Vasil'eva, N.M. Katashuk, T.V. Snegiryova, and B.I. D'yachenko, *Vysokomolek. Soed.*, **A18**, No. 6, 1270-1275 (1976).
17. K.A. Andrianov, T.V. Vasil'eva, V.D. Deeva, N.M. Katashuk, and B.I. D'yachenko, *Vysokomolek. Soed.*, **A19**, No. 1, 167-172 (1977).
18. K.A. Andrianov, N.M. Petrovnina, T.V. Vasil'eva, V.E. Shklover, and B.I. D'yachenko, *Zh. Obshch. Khimii*, 48, No. 12, 2692-2694 (1978).
19. T.V. Vasil'eva, N.M. Petrovnina, N.G. Ufimtsev, and B.S. Kirillov, *Plast. massy*, No. 5, 13-14 (1981).
20. T.V. Vasil'eva and V.N. Ryzhov, *Abstr. V USSR Conf. on Chemistry and Application of Organosilicon Compounds*, Tbilisi, 1980, p. 302 (in Russian).
21. K.A. Andrianov, *Methods of Organoelement Chemistry. Silicon.* Moscow, Nauka, 1968 (in Russian).
22. Yu.I. Rastorguev, E.A. Ryabenko, and A.I. Kuznetsov, *Zh. Prikl. Khimii*, **50**, No. 4, 2602 (1977).
23. Yu.I. Rastorguev, A.I. Kuznetsov, and M.V. Mikheev, *Zh. Prikl. Khimii*, **54**, No. 9, 2111 (1981).

24. Yu.I. Rastorguev, A.I. Kuznetsov, and M.V. Mikheev, *Zh. Prikl. Khimii*, 55, No. 1, 218 (1982).
25. V.M. Kopylov, A.V. Voronkov, S.K. Zinovich, G.M. Tseitlin, V.V. Kireev, and I.M. Kostylyov, *Vysokomolek. Soed.*, **A27**, No. 2, 346-351 (1985).
26. V.M. Kopylov, A.V. Voronkov, G.M. Tseitlin, V.V. Kireev, and S.K. Zinovich, *Vysokomolek. Soed.*, **A26**, No. 8, 1706 (1984).
27. V.M. Kopylov, A.V. Voronkov, V.V. Kireev, G.M. Tseitlin, S.K. Zinovich, and I.M. Kostylyov, *Vysokomolek. Soed.*, **B26**, No. 10, 789 (1984).
28. H. Mark and A.W. Tobolsky, *Physical Chemistry and High Polymer Substances*, New York-London, Interscience Publ. Inc., 1950, Ch. IX, p. 61.
29. L.B. Sokolov, *Fundamentals of Polymer Synthesis by Polycondensation*, Moscow, Khimiya, 1979 (in Russian).
30. P.V. Ivanov, N.I. Gal'perin, and V.V. Kireev, *Vysokomolek. Soed.*, **A28**, No. 5, 1041-1046 (1985).
31. P.V. Ivanov, N.I. Gal'perin, and V.V. Kireev, *Khim. Prom-st*, No. 7, 60-61 (1985).
32. V.V. Kireev, T.V. Vasil'eva, P.V. Ivanov, and G.N. Yakovleva, *Abstr. USSR Sci.-Tech. Conf. on Service Properties of Structural Polymer Materials*, Nalchik, 1984, Part I, 19 (in Russian).
33. T.V. Vasil'eva, V.Ya. Stolyarenko, G.N. Yakovleva, and V.V. Yastrebov, *Zh. Obshch. Khimii*, 52, No. 11, 2570 (1982).
34. France Patent 1472047, 1967.
35. R. Iler, *The Chemistry of Silica*, New York, John Wiley and Sons, 1979.
36. M.S. Aslanova, B.I. D'yachenko, D.Ya. Zhinkin, V.P. Rybalko, T.V. Vasil'eva, *et. al.*, USSR Inventor's Certificate 861358, *Byull. izobr.* No. 33 (1981).
37. V.P. Rybalko, *Abstr. Production and Reprocessing of Plastics and Synthetic Resins*, Moscow, NIITEKhIM, No. 2, 39-42 (1981) (in Russian).
38. K.A. Andrianov, B.A. Kamaritsky, B.I. D'yachenko, and V.D. Nedorosol, *Dokl. Akad. Nauk SSSR*, 225, No. 5, 1135 (1975).
39. V.V. Kireev, B.I. D'yachenko, and V.P. Rybalko, *Some Aspects of Hydrolytic Polycondensation of Highly Functional Organochlorosilanes, Abstr. XXII USSR Conf. on High Molecular Weight Compounds*, Alma-Ata, 1985 (in Russian).
40. V.P. Rybalko, B.I. D'yachenko, T.V. Vasil'eva, G.I. Polinsky, S.R. Stepanenko, and N.M. Petrovnina, *Abstr. V USSR Conf. on Chemistry and Application of Organosilicon Compounds*, Tbilisi, 1980, p. 285 (in Russian).
41. V.P. Rybalko, E.F. Fedotova, L.S. Mel'nichenko, B.I. D'yachenko, and V.V. Kireev, *New Binders for Reinforced Plastics. Coll. of papers*, Moscow, VNIISPB, 1982, p. 40 (in Russian).
42. V.V. Kireev, V.P. Rybalko, V.A. Savin, B.I. D'yachenko, N.P. Erokhina, Yu.M. Talanov, A.D. Gut'ko, and N.K. Vikulova, *Abstr. II USSR Conf. on Composite Materials and Their Applications*, Tashkent, 1983, p. 124 (in Russian).
43. B.I. D'yachenko, N.K. Vikulova, V.P. Rybalko, V.V. Kireev, S.R. Stepanenko, Yu. M. Talanov, A.D. Gut'ko, and E.B. Gubina, *Dokl. Akad. Nauk SSSR*, 271, No. 6, 1425 (1983).
44. V.V. Kireev, B.I. D'yachenko, V.P. Rybalko, R.A. D'yachenko, and G.I. Polinsky, *Abstr. II USSR Conf. on Composite Materials and Their Applications*, Tashkent, 1983, p. 125.
45. Yu.A. Yuzhelevsky, E.G. Kagan, N.P. Timofeeva, T.D. Doletskaya, and A.L. Klebansky, *Vysokomolek. Soed.*, **A13**, No. 1, 183 (1973).
46. M. Mazurek, M. Sciborek, J. Chojnowsci, B.G. Zavin, and A.A. Zdanov, *Europ. Polymer. J.*, 66, No. 1, 67-69 (1980).
47. M.G. Voronkov, V.P. Mileshkevich, and Yu.A. Yuzhelevsky, *Siloxane Linkage*, Novosibirsk, Nauka, 1976 (in Russian).

48. V.M. Kopylov, D.Ya. Zhinkin, P.L. Prikhod'ko, A.M. Gasanov, and V.A. Kovyazin, *Vysokomolek. Soed.*, **A23**, No. 3, 651-657 (1981).
49. H. Schmidbauer and A.H.S. Perez-Garsia, *Z. Anorg. Allg. Chem.*, **328**, 105-112 (1964).
50. I.L. Dubchak, V.E. Shklover, M.Yu. Antipin, Yu.T. Struchkov, V.M. Kopylov, P.L. Prikhod'ko, and A.A. Zhdanov, *Zh. Strukt. Khimii*, **23**, No. 2, 63-71 (1982).
51. I.L. Dubchak, V.E. Shklover, Yu.T. Struchkov, V.M. Kopylov, and P.L. Prikhod'ko, *Zh. Strukt. Khimii*, **24**, No. 2, 59-63 (1983).
52. V.M. Kopylov, P.L. Prikhod'ko, V.A. Kovyazin, and I.L. Dubchak, *Vysokomolek. Soed.*, **A26**, No. 9, 1882-1887 (1984).
53. K.A. Andrianov, A.I. Chernyshev, V.A. Temnikovsky, V.V. Yastrebov, and V.M. Kopylov, *Teor. i Eksper. Khimiya*, **11**, 678-681 (1975).
54. K.A. Andrianov, A.I. Chernyshev, P.L. Prikhod'ko, and S.E. Esipov, *Zh. Obshch. Khimii*, **50**, No. 5, 1044 (1980).
55. K.A. Andrianov, V.M. Kopylov, P.L. Prikhod'ko, and V.A. Temnikovsky, *Abstr. I USSR Symposium on Structure and Reactivity of Organosilicon Compounds, Irkutsk*, 1977, pp. 274-275 (in Russian).
56. V.M. Kopylov, P.L. Prikhod'ko, and V.A. Temnikovski, *6th International Symposium on Organosilicon Chemistry, Abstracts of Papers*, Budapest, 1981, p. 163.
57. K.A. Andrianov, E.I. Khubulava, V.M. Kopylov, L.M. Khananashvili, A.I. Nogaideli, and G.E. Stakhrovskaya, *Dokl. Akad. Nauk SSSR*, **233**, 354-357 (1977).
58. L.M. Khananashvili, V.M. Kopylov, E.I. Khubulava, and G.E. Stakhrovskaya, *Soobshcheniya Akad. Nauk Gruz. SSR*, 98, No. 2, 333-336 (1980).
59. K.A. Andrianov, A.I. Nogaideli, E.I. Khubulava, V.M. Kopylov, L.M. Khananashvili, A.G. Kolchina, and N.G. Sychyova, *Vysokomolek. Soed.*, **A18**, No. 2, 2619-2625 (1976).
60. K.A. Andrianov, A.L. Nogaideli, V.M. Kopylov, E.I. Khubulava, and A.G. Kolchina, *Soobshcheniya Akad. Nauk Gruz. SSR*, 94, 362-364 (1976).
61. V.M. Kopylov, E.I. Khubulava, N.G. Sychyova, *Abstr. IUPAC Intern. Symp. on Macromolecular Chemistry*, Tashkent, 1978, vol. 2, p. 184.
62. V.M. Kopylov, P.L. Prikhod'ko, and V.A. Kovyazin, *Vysokomolek. Soed.*, **A24**, No. 8, 1751 (1982).
63. K.A. Andrianov, V.M. Kopylov, V.A. Temnikovsky, and L.M. Khananashvili, *Vysokomolek. Soed.*, **A18**, No. 8, 1714-1720 (1976).
64. K.A. Andrianov, Yu.R. Valnieks, V.M. Kopylov, G.Ya. Rumba, and L.M. Khananashvili, *Vysokomolek. Soed.*, **B21**, No. 1, 63-66 (1979).
65. G.L. Lee, G.L. Frye, and O.K. Johanson, *Polymer. Prepr.*, **10**, No. 2, 1361 (1969).
66. Yu.A. Yuzhelevsky, A.S. Shapatin, Yu.L. Kaufman, N.N. Fedoseeva, P.G. Ten, and D.Ya. Zhinkin, *Vysokomolek. Soed.*, **B13**, No. 12, 904 (1971).
67. K.A. Andrianov, E.I. Khubulava, V.A. Temnikovsky, V.M. Kopylov, A.I. Nogaideli, and L.M. Khananashvili, *Dokl. Akad. Nauk SSSR*, 229, 614-617 (1976).
68. M.G. Voronkov, and L.A. Zhagata, *Zh. Obshch. Khimii*, 37, No. 11, 2764-2765 (1967).
69. C.S. Kreihanzel and E.J. Poist, *J. Organomet. Chem.*, 8, 239 (1967).
70. R.B. Müller and T. Reichenback, *Tetr. Lett.*, 543-546 (1974).
71. T.M. Chan and W. Michailowsky, *Tetr. Lett.*, 3479-3482 (1974).
72. T.M. Chan, P.W.R. Lan, and M.P. Li, *Tetr. Lett.* 2067-2071 (1976).
73. I.A. Vasilenko, G.A. Serebryannikova, and R.P. Evstigneeva, USSR Inventor's Certificate No. 466209, *Byull. isobr.*, No. 13, 51 (1975).
74. I.A. Vasilenko, G.A. Serebryannikova, and R.P. Evstigneeva, *Bioorganich. Khimiya*, **1**, 56 (1975).

75. M.A. Sokolova, B.I. Mitsner, N.Yu. Gorina, and R.P. Evstigneeva. USSR Inventor's Certificate No. 548595, *Byull. izobr.*, No. 8, 93 (1977)
76. K.A. Andrianov, and L.M. Tartakovskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 11, 2631-2632 (1972).
77. I.S. Akhrem, M.Dyone, and M.E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 4, 932-934 (1973).
78. M. Deneux, J.C. Akhrem, A.D. Avetissian, E.J. Mussoff, and M.E. Vol'pin, *Bull. Soc., Chim. France*, Part 1, 2638-2642 (1973).
79. J. Boyer, R.J.P. Corrin, R. Perz, and C. Reye, *J. Organomet. Chem.*, **148**, C1-C4 (1978).
80. K.A. Andrianov, L.I. Tartakovskaya, V.M. Kopylov, and Zh. N. Sementsova, *Zh. Obshch. Khimii*, 45, No. 1, 112-116 (1975).
81. K.A. Andrianov, L.M. Tartakovskaya, V.M. Kopylov, and L.M. Sarafanova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 6, 1443-1445 (1975).
82. K.A. Andrianov, L.M. Tartakovskaya, and V.M. Kopylov, *Abstr. IV Internat. Symp. on Chemistry of Organosilicon Compounds*, Moscow, 172, 1975.
83. A.A. Zhdanov, L.M. Tartakovskaya, V.M. Kopylov, I.G. Makarov, and V.M. Kazakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 12, 2818-2820 (1980).
84. L.M. Tartakovskaya, V.M. Kopylov, and A.A. Zhdanov, *Abstr. II USSR Symp. on Structure and Reactivity of Organosilicon Compounds, Irkutsk*, 1981, p. 156 (in Russian).
85. L.M. Tartakovskaya, V.M. Kopylov, and A.A. Zhdanov, *Vysokomolek. Soed.*, **B26**, No. 3, 234-238 (1984).
86. P.L. Prikhod'ko, V.M. Kopylov, L.M. Tartakovskaya, and A.A. Zhdanov, *Vysokomolek. Soed.*, **A26**, No. 9, 1988-1992 (1984).
87. V.V. Severny, R.M. Minas'yants, and O.I. Minas'yants, *Vysokomolek. Soed.*, **A19**, No. 7, 1549-1555 (1977).
88. V.V. Severny, R.M. Minas'yants, V.V. Sokolov, and A.V. Kisin, *Kauchuk i Rezina*, No. 2, 14-16 (1976).
89. B.V. Molchanov, D.Ya. Zhinkin, O.G. Ryzhova, G.G. Solovei, E.A. Chuprova, I.A. Makarenko, and A.I. Sbrodov, Dep. rukopis, NIITEKhIM, No. 481, XII-D-81 (1981); RZhKhIM, 17T406 (1981).
90. A.Ya. Malkin, S.G. Kulichikhin, E.Ya. Naroditskaya, V.Ya. Pozdnyakov, I.N. Yunitsky, and V.V. Kireev, *Vysokomolek. Soed.*, **A27**, No. 10, 2040-2047 (1985).
91. E.Ya. Naroditskaya, I.D. Khodzhayeva, S.G. Kulichikhin, V.Ya. Pozdnyakov, I.N. Yunitsky, V.V. Kireev, and A.Ya. Malkin, *Vysokomolek. Soed.*, **B27**, No. 9, 713-716 (1985).
92. I.V. Sevast'yanova, V.P. Davydova, Zh.N. Kostyakova, and A.V. Karlin, *Kauchuk i Rezina*, No. 1, 24-26 (1981).
93. P. Flory, *Macromolecules*, **12**, No. 1, 119-122 (1979).
94. L.Z. Rogovina, V.G. Vasil'yev, G.L. Slonimsky, *Vysokomolek. Soed.*, **A24**, No. 2, 254 (1982).
95. V.V. Kireev, G.S. Kolesnikov, I.M. Raigorodsky, P.O. Okulevich, *Zh. Obshch. Khimii*, **41**, No. 4, 792-797 (1971).
96. T.N. Beloglazova, V.V. Kireev, G.S. Kolesnikov, and I.M. Raigorodsky, *Vysokomolek. Soed.*, **A13**, No. 6, 1625-1629 (1971).
97. L.Yu. Mal'kevich and V.V. Kireev, *Vysokomolek. Soed.*, **B15**, No. 8, 617 (1973).
98 V.V. Kireev, V.I. Astrina, and A.A. Goryaev, *Zh. Obshch. Khimii*, 52, No. 3, 473-478 (1982).
99. V.I. Astrina, V.V. Kireev, and L.A. Savchenko, *Vysokomolek. Soed.*, **B24**, No. 6, 792-795 (1982).
100. V.V. Kireev, S.O. Shumakova, and A.A. Izyneev, *Abstr. V USSR Conf. on Chemistry and Applications of Organosilicon Compounds*, Tbilisi, 1980, p. 197.

101. V.V. Kireev, S.O. Shumakova, and A.A. Izyneev, *Dep. VINITI* No. 1729-79, RZhKh, 15C35OD (1979).
102. V.V. Kireev, S.O. Shumakova, and G.I. Mitropol'skaya, *Condensation Block Copolymers*, Coll. of papers, Nal'chik, 32-38 (1982) (in Russian).
103. V.V. Kireev, V.A. Kovyazin, V.M. Kopylov, M.G. Zaitseva, and I.M. Kostylev, *Zh. Obshch. Khimii*, **54**, No. 2, 361-365 (1984).
104. V.V. Kireev, V.A. Kovyazin, V.M. Kopylov, M.G. Zaitseva, and G.I. Mitropol'skaya, *Zh. Obshch. Khimii*, **54**, No. 8, 1899-1904 (1984).
105. Yu.E. Ovchinnikov, V.E. Shklover, Yu.T. Struchkov, A.A. Remizova, V.A. Kovyazin, V.M. Kopylov, and V.V. Kireev, *Z. Anorg. Allg. Chem.*, 523, 14-20 (1985).
106. K.A. Andrianov, M.M. Il'in, V.N. Talonov, M.V. Konstantinova, and V.V. Kazakova, *Zh. Obshch. Khimii*, **47**, No. 7, 1758 (1977).
107. K.A. Andrianov, M.M. Il'in, V.N. Talonov, M.V. Konstantinova, and I.I. Zhurakovskaya, *Vysokomolek. Soed.*, **B19**, No. 2, 128 (1977).
108. K.A. Andrianov, V.N. Talanov, L.M. Khananashvili, N.P. Gashnikova, M.M. Il'in, and N.A. Sidorenko, *Dokl. Akad. Nauk SSSR*, **198**, No. 1, 87 (1971).
109. K.A. Andrianov, M.M. Il'in, V.N. Talanov, L.S. Isakova, and N.A. Sidorenko, *Vysokomolek. Soed.*, **A18**, No. 11, 2752 (1976).
110. K.A. Andrianov, M.M. Il'in, V.N. Talanov, and I.I. Zhurakovskaya, *Izv. Akad. Nauk SSSR*, No. 11, 2614 (1976).
111. K.A. Andrianov, M.M. Il'in, M.V. Konstantinova, and V.V. Kazakova, *Zh. Obshch. Khimii*, **49**, No. 2, 346 (1979).
112. K.A. Andrianov, M.I. Shkol'nik, V.M. Kopylov, and P.L. Prikhod'ko, *Dokl. Akad. Nauk SSSR*, **227**, No. 2, 352 (1976).
113. V.A. Mazayev, V.N. Talanov, M.M. Il'in A.K. Tsapuk, L.S. Miklin, and T.N. Domashenko, *Izv. Akad. Nauk SSSR, neorganich. materialy*, **19**, 2044 (1983).
114. K.A. Andrianov, N.A. Tebeneva, I.M. Petrova, and G.V. Kotrelev, *Dokl. Akad. Nauk SSSR*, **222**, No. 5, 1101 (1975).
115. D.Ya. Zhinkin, V.M. Kopylov, I.S. Shragin, Zh.S. Syrtsova, N.M. Alekseeva, *Vysokomolek. Soed.*, **A23**, No. 8, 1776-1782 (1981).
116. D.Ya. Zhinkin, I.S. Shragin, V.M. Kopylov, Zh.S. Syrtsova, V.V. Yastrebov, M.G. Zaitseva, *Vysokomolek. Soed.*, **A22**, No. 7, 1541-1549 (1980).
117. K.A. Andrianov, G.V. Kotrelev, N.A.Tebeneva, N.V. Pertsova, I.I. Tverdokhlebova, P.A. Kurginyan, T.A. Larina, and E.G. Khoroshilova, *Vysokomolek. Soed.*, **A20**, No. 3, 692-699 (1978).
118. K.A. Andrianov, I.I. Tverdokhlebova, S.S.-A. Pavlova, T.A. Larina, P.A. Kurginyan, G.V. Kotrelev, N.A. Tebeneva, N.V. Pertsova, and E.G. Khoroshilova, *Vysokomolek. Soed.*, **A19**, No. 10, 2300-2304 (1977).

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